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RESEARCH

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4 Vols.

by R P Rastogi and B N Mehrotra

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Vol.3 1993. Pp 831. Price Rs 600; Postage Rs 15.
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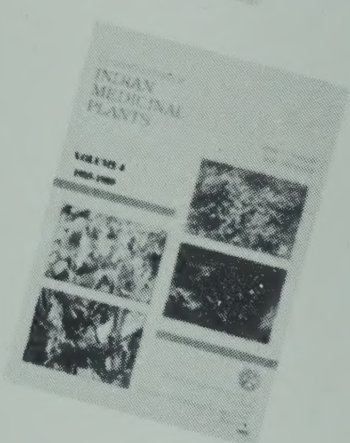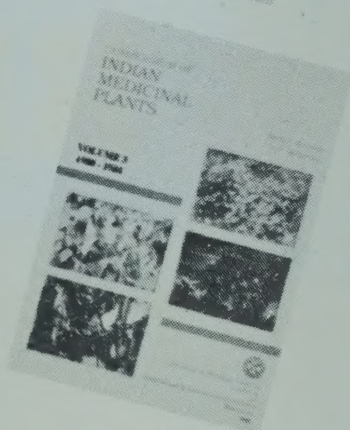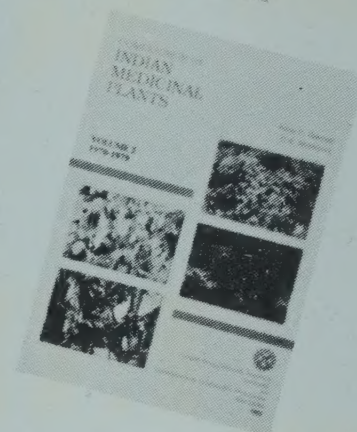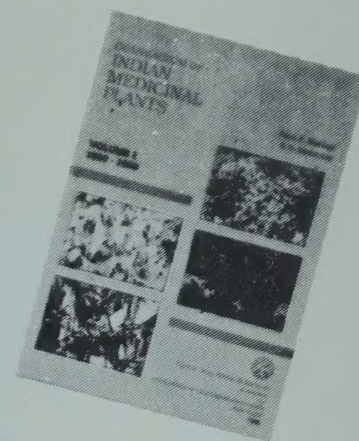
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Controlled Free Radical Polymerization

S. Sivaram

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Precise control of macromolecular structure and architecture continues to be a dominant theme of contemporary polymer research. Amongst the armoury of polymerization techniques available to polymer chemists, free radical polymerization is the oldest, most studied and extensively exploited in commercial practice. Nevertheless, free radical polymerizations have been most difficult to control and are generally characterized by broad molecular weight distribution, poor control of molecular weights and chain end functionality and inability to synthesize well-defined block copolymers.However, polymer chemists have, in recent years, succeeded in effectively controlling the free radical polymerization by invoking the concept of reversible termination involving an active species in rapid equilibrium with a dormant species. Using controlled free radical polymerization it is feasible to produce poly(styrene)s with polydispersities as low as 1.05 with good control of molecular weight. Furthermore, a variety of novel end functionalized polymers as well as random, block, graft, star and hyperbranched polymers have been prepared using controlled free radical polymerization. The paper reviews the explosive developments in this area since the appearance of the first publication in 1993. The scope of this new technique for polymer synthesis is illustrated with representative examples.

Introduction

Precise control of macromolecular structure and architecture continues to be a dominant theme of contemporary polymer research[1]. Fundamental to this endeavour is the availability of synthetic methods capable of providing a high degree of control on the primary bond making and bond breaking events that determine the course of a polymerization reaction, namely, chain initiation, propagation, transfer and termination[2]. Ideally speaking, after the chains are initiated, the chains should only continue to propagate without undergoing any chain breaking events such as transfer or termination process. Under these ideal conditions, the polymer growth reaction can be termed as highly "chemoselective", wherein the growing active center adds only to another monomer. High chemoselectivity in polymerization defines the size of the macromolecule, the uniformity of molecular weight and determines the ability to manipulate the terminal end of the polymer chain. If initiation is fast, then the degree of polymerization is uniquely defined by the ratio of the concentration of reacted monomer to that of the added initiator, namely, $DP_n = [M]/[I_o]$. Such a chemoselective polymerization has been called living polymerization in polymer science alluding to the existence of a reactive chain end during the course of the polymerization.

Living Anionic Polymerizations

Living polymerizations were first experimentally observed in chain reactions involving a carbanion as the growing end (anionic polymerization)[3]. Under conditions, wherein adventitious impurities are rigorously excluded, a carbanion chain end undergoes only propagation reaction with the complete absence of any termination or transfer process. In these systems, chain ends also do not react with one another due to electrostatic repulsions. Various ideal living systems have been described for alkenes and dienes polymerization as well as for ring opening polymerization of epoxides. Although less satisfactory, they have been extended to even more difficult systems such as polymerization of methacrylates (enolate chain ends)[4] and metathesis polymerization (metal-

locarbene chain ends)[5]. The living anionic polymerization systems have been recently reviewed[6].

Controlled Cationic Polymerization

Extension of these concepts to a cationic chain end (carbocationic polymerization) proved difficult. Spontaneous and facile elimination of hydrogen (as proton) from the β-carbon of the growing carbocation was thought to be a formidable obstacle to achieve livingness in cationic polymerization. However, the progress in better understanding of the behaviour of carbocations and the correct choice of experimental conditions led to better degree of control. The logic of the approach rested on the following premise. Kinetically, at high initiator concentrations ($[I_o] \geq 10^{-2}$ mol L^{-1}) the occurrence of transfer due to β- hydrogen elimination is not very prominent. Therefore, if initiation is fast, it is still possible to avoid or minimize the transfer reaction using a high initiator concentration. However, carbocations are very reactive towards alkene ($R_P \sim 10^5$ mol^{-1} L s^{-1} at $\sim 20°C$) and hence at high concentration of initiator (high carbocation concentration), the polymerization reaction will be uncontrollable. In order to reduce the rate of polymerization, it was proposed that the active carbocation should be in equilibrium with a dormant species with a fast and reversible equilibrium between the two species. Under such conditions, the number of chains (and hence $\overline{M}n$) will be determined by the total concentration of active and dormant species whereas the rate of polymerization will be proportional to the low concentration of the active species in equilibrium ($[C^*] \sim 10^{-7}$ mol L^{-1})[7].

Experimental conditions were defined for the controlled polymerization of styrene, isobutyl vinylether and isobutylene using cationic initiators[8]. These polymerizations are not ideally living since they possess a finite transfer and termination rate. But by appropriate choice of reaction conditions, their contributions to the polymer growth reaction can be minimized. Nevertheless, from a practical point of view the controlled polymerization is still useful in the sense that it can produce polymers with predetermined molecular weights, low polydispersity and controlled functionality. Furthermore, if after the consumption of the first monomer (A), a second monomer (B) is added, the polymerization will reinitiate again leading to a block copolymer of the type $(A\text{-}A\text{-}A)_m (B\text{-}B\text{-}B)_n$.

Controlled Free Radical Polymerization

If, on the contrary, the growing chain ends are free radicals, there are two potentially damaging reactions, which render the possibility of a living radical polymerization still more difficult.. These are radical coupling and disproportionation. Of the two, fast termination of chain end by radical coupling is the most important chain breaking event in free radical polymerization. The importance of radical coupling increases with the concentration of growing species since termination is second order with respect to growing radical whereas propagation is first order. Thus the proportion of deactivated chains (dead chains) increases with increasing chain length. Furthermore, radical polymerization is characterized by slow initiation (and hence low stationary concentration of growing radical) and fast propagation.

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In view of these considerations, attempts to achieve controlled free radical polymerization of monomers were largely unsuccessful in the past. However, it was recognized that free radical polymerization is one of the most important commercial process for the synthesis of a host of useful materials. The number of monomers amenable to free radical polymerization is potentially large. Also, free radical polymerization occurs at 25 to 100° C and most often in water, as suspension, solution or emulsion. This is in contrast to ionic polymerization which often requires expensive organic solvents, complete exclusion of moisture and oxygen (< 10 ppm) and temperatures lower than ambient. Therefore, there exists strong motivation for extending the concept of living and controlled polymerization from ionic to radical process. This would enable synthesis of new materials with novel characteristics (functional polymers, block, graft and branched polymers/copolymers) from the readily available monomers using less expensive reaction conditions.

The most promising approach was to extend the principles underlying the controlled carbocationic polymerization to free radical polymerization. Thus, a method was sought by which one could ensure a low momentary or stationary concentration of growing radicals in solution. In other words, the objective was to render the radical less free. Furthermore, to ensure narrow polydispersity, the rate of initiation should be at least equal to or greater than the rate of propagation. However, there is one major difference between polymerizations propagating through carbocations and free radicals. Addition of the latter to a double bond is far too slow compared to the former; and if one considers the low stationary concentration of the growing radical, it can be anticipated that the controlled radical polymerization will be too slow for any practical applications. Based on the estimate of k_p and k_t at 60°C, it can be estimated that for styrene at $[M]_o = 1$ mol L^{-1} and for synthesizing a polymer with a DP$_n$ = 100, it will take more than one year to reach 99% conversion, if the stationary concentration of growing radicals is assumed to be 10^{-9} mol L^{-1}!

Nevertheless, the situation is not so hopeless. The rates of polymerization can be improved by accepting lower conversions, some finite termination of the growing radicals and by operating at higher monomer concentrations (higher stationary concentration

of radicals). Polymerization at higher temperature has a favourable effect on ratio k_p/k_t, since the activation energy for propagation is always higher than that of termination. The choice of the monomer is also a factor to be reckoned with. The k_p/k_t ratio increases in the order ethylene (0.0005 x 10^{-4}) < styrene (0.03 x 10^{-4}) < methyl methacrylate (0.2 x 10^{-4}) < vinyl acetate (10^{-4}) < methyl acrylate (2.1 x 10^{-4}). Thus, with methyl acrylate one can operate at 70-times higher stationary concentration of growing radicals compared to styrene on account of the more favourable k_p/k_t ratio[9].

Based on the above kinetic frame-work, it is possible to understand the burgeoning literature on controlled free radical polymerization of vinyl monomers. Essentially literature uses two major approaches to ensure low stationary concentration of growing radical. One, use of a radical scavenger which would reversibly combine with a growing radical, but by itself would not add to the double bond and second, use a suitable transition metal compound which could reversibly complex with a growing radical and provide the necessary dormant species in equilibrium with the growing radical[10].

One of the first examples of a controlled polymerization of vinyl monomer using free radical chemistry is due to Otsu and Yashida[11] have shown that certain compounds (e.g. tetramethylthiuram disulfide) when heated, fragment to form two dithiocarbomate radicals which act both as primary radicals to initiate polymerization and as also radical chain transfer agents and terminators (iniferters). Chain growth results from the repeated breaking of the polymer chain dithiocarbamate bond, addition of monomer followed by termination by the dithiocarbamate radical. Molecular weight increased in a linear fashion with reaction period and conversion. This result can be contrasted with a conventional free radical polymerization process in which high molecular weight is obtained early in the reaction and remains more or less constant until the gel effect occurs[12]. The polymerization obeys a first order kinetics in monomer as often observed for stationary state kinetics. However, these reactions do not qualify for being termed as living or controlled since they neither produce narrow polydispersity nor permit synthesis of polymers with predetermined molecular weights. Nevertheless, Nair and Clouet[13] creatively

exploited this chemistry to make end functionalized polymers and diblock/multiblock copolymers by suitable choice of the iniferters. Many other initiators with features similar to those exhibited by iniferters have been reported in the literature. However, none of these reactions would rigorously satisfy all the criteria needed to qualify them as living or controlled polymerization.

Reversible Combination of Radicals with Stable Free Radicals

The first example of a controlled free radical polymerization using a stable free radical (SFR) as a radical scavenger to reversibly combine with a growing radical appeared in 1993 and is due to the work of Georges et al.[14] at Xerox Research Center, Canada. They used a nitroxide stable radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to form weak adducts in dynamic equilibrium with the growing styryl radical. The advantage of stable free radicals like TEMPO is that they themselves do not add to double bond. Using benzoyl peroxide (BPO) as initiators at 123°C, styrene was polymerized in bulk (TEMPO/BPO = 1.2) to give a 90% conversion to poly(styrene) after 70 hours with a $\overline{M}n = 7800$ and $\overline{M}w = 10,000$ and a $\overline{M}w/\overline{M}n = 1.27$. $\overline{M}n$ increased linearly with time and conversion (up to 70%). Increasing TEMPO/BPO ratio to 3, resulted in reduced conversion and molecular weight. However, polydispersity values became narrower. The polymerization rate was first order in monomer concentration.

These results are indicative of a lower stationary concentration of the growing polystyryl radical in dynamic equilibrium with a thermally labile adduct of the polystyryl radical with TEMPO. Fortuitously, it was observed that addition of camphor sulfonic acid (CSA) caused a dramatic increase in the rate of polymerization as well as molecular weight[15]. There was a slight broadening of polydispersity. Typically, it was shown that heating a mixture of CSA (0.018g) with TEMPO (0.013g) and BPO (0.015g) in styrene (36g) at 127°C gave a poly(styrene) with $\overline{M}w = 147,412$, $\overline{M}n = 107,556$ and $\overline{M}w/\overline{M}n = 1.37$. CSA, presumably, reduces the autopolymerization of styrene, which, competes with stable free radical mediated polymerization, leading to broadening of molecular weight distribution. More recently, 2-fluoro-1-methylpyridinium p-toluenesulfonate has

been demonstrated to result in a greater enhancement of the rate of polymerization compared to CSA, without broadening the molecular weight distribution[16]. The mechanism of action of this compound is yet unclear.

The approach has been successfully applied not only to bulk homopolymerization and block copolymerization but also to suspension copolymerization and emulsion homopolymerization.

The feasibility of preparing a stable, isolable polystyrene end capped with a nitroxide stable free radical was demonstrated. It was shown that this dormant species upon heating with fresh styrene, undergoes chain extension with slight broadening of molecular weight distribution[17]. Such nitroxyl end capped polymers were considered as suitable precursors for the preparation of block copolymers.

One of the competing processes that needs to be considered while conducting a free radical initiated styrene polymerization at 140-150°C is the autopolymerization. Autopolymerization of styrene has been extensively studied and is believed to occur by the Mayo mechanism[18]. The primary step in this mechanism is the Diels-Alder type reaction between two styrene molecules leading to an intermediate which by a two electron transfer process generates the free radicals necessary for the initiation of polymerization (Scheme 1). It has been reported that strong acids (e.g. camphor sulfonic acid (CSA) can convert the Diels Alder product into the innocuous product and thus inhibit autopolymerization. Recent studies by Georges et al.[19] have shown that benzoic acid is a more potent inhibitor of autopolymerization.
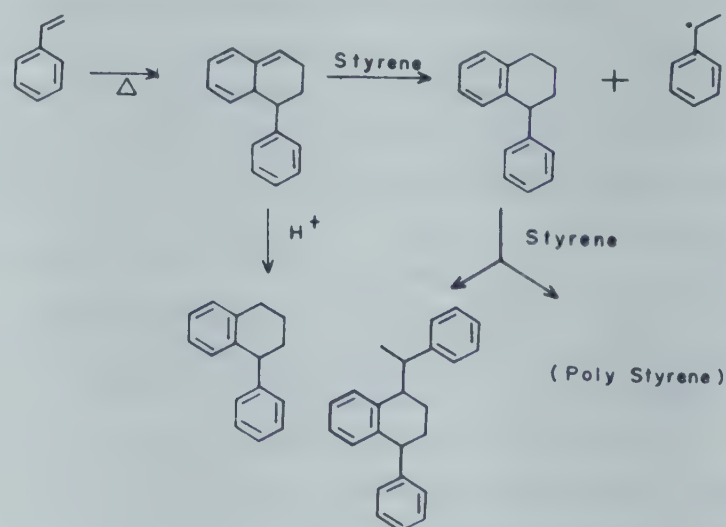
Scheme 1 — Mechanism of autopolymerization of styrene

Autopolymerization of styrene at 130°C in the presence of TEMPO and benzoic acid gave after 39 h, poly(styrene) with $\overline{M}w$ 10326 and $\overline{M}n$ 7304 and $\overline{M}w/\overline{M}n$ = 1.41 (58% conversion). Under identical conditions but without benzoic acid poly(styrene) with $\overline{M}n$ = 1658, $\overline{M}w$ = 4289, $\overline{M}w/\overline{M}n$ = 2.58 (32% conversion) was obtained. Autopolymerization of styrene at 130° could be inhibited by benzoic acid up to 15 h.

Addition of CSA increases the molecular weight but also causes broadening of polydispersity. Peroxide initiated styrene polymerization gave the narrowest polydispersity. Thus, the choice of BPO as initiator turned out to be fortuitous since, benzoic acid is produced *in situ* during the thermal decomposition of BPO. The primary rate enhancement mechanism due to organic acids, such as CSA, in nitroxide mediated polymerizations is proposed to involve the consumption of nitroxide radicals. The resulting reduction in nitroxide concentration affects the equilibrium between growing and dormant chains, increasing the number of growing chains, and hence the polymerization rate[20].

However, conflicting results have been reported by Matyjaszewski and coworkers[10]. They showed that addition of 0.02 - 0.12 M TEMPO to bulk polymerization of styrene at 120°C, resulted in a linear plot of $\overline{M}n$ versus conversion. The reaction was characterized by an induction period which decreased with increasing TEMPO concentration. $\overline{M}n$ up to 10,000 with polydispersity of 1.2 - 1.3 could be achieved. Polydispersity tend to broaden with increasing conversion. Thus, narrow polydispersity resins could be obtained even in the absence of any acid additives. The amount of scavenger was reported to control polymerization rates and molecular weights.

Styrene polymerization can also be initiated by azo-bis- isobutyronitrile (AIBN) in the presence of TEMPO. However, rates of polymerization were slower than BPO[10].

Modification in the structure of the stable free radical has a significant effect on the course of AIBN initiated polymerization of styrene at 120°C. 4-Phosphonoxy-TEMPO produced higher rates and higher molecular weight compared to TEMPO whereas 4-hydroxy TEMPO depressed both rate and molecular weight[10]. Using a more complex coordinated nitrox-

ides, styrene polymerization was reported even at 80°C. Under similar conditions polymerization of vinyl acetate, methyl acrylate and methyl methacrylate were faster than styrene (bulk, AIBN, 0.03 M : TEMPO, 0.03M).

Nitroxide mediated stable free radical polymerization has been extended to the aqueous phase polymerization of sodium styrene sulfonate[21]. The polymerization was performed in 80% by volume aqueous ethylene glycol, using $K_2S_2O_8$/Na HSO_3 as the initiator ($[M]_o$ = 0.146 mol, $[I]_o$ = 6 mM $K_2S_2O_8$, 8 mM $NaHSO_3$, [TEMPO]$_o$ = 12 mM 120°C, 4h). The conversion to polymer was 96%, $\overline{M}n$ = 23000 and $\overline{M}w/\overline{M}n$ = 1.35. It was possible to isolate the nitroxide terminated poly(styrenesulfonic acid) ($\overline{M}n$ 8000, $\overline{M}w/\overline{M}n$ = 1.08) as a solid powder, which upon redissolving in an aqueous EG solution containing additional monomer reinitiated the polymerization. Thus, the chain end is not only living, it is also isolable and can be even stored!

It has been shown that the nitroxide mediated stable free radical polymerization does not show any gel or Tromsdorff effect because of the living nature of polymerization[22]. The mechanism of living free radical polymerization using nitroxide radicals indicate that the polymerization is first order in monomer concentration. Furthermore, the termination of polymer chains by radical combination is greatly reduced[23]. Results obtained with bulk polymerization of styrene using stable free radicals are summarized in Table 1.

Mardare *et al.*[24] reported that methyl methacrylate (MMA) could be polymerized in a controlled manner using an organoaluminum compound complexed with a stable free radical in the presence of a bidentate Lewis base. For example, use of triisobutyl aluminum in conjunction with TEMPO or TEMPO and bipyridyl caused a rapid polymerization of MMA at 25°C in benzene. The semilogarithmic time - conversion plot was linear, indicating a constant concentration of active species. However, only the tricomponent system showed a linear increase in $\overline{M}n$ conversion with a polydispersity of 1.25. The initiator efficiency (Ieff) was 0.68. A maximum $\overline{M}n$ = 15000 was reported under these conditions. A radical mechanism involving the growing PMMA radicals reversibly stabilized by a neutral tri or pentacoordinated aluminum derivative was proposed.

Table 1 — Bulk polymerization of styrene using TEMPO/BPO

Sl no.	Styrene, g (mol)	BPO, g (mmol)	TEMPO, g (mmol)	Acid, g (mmol)	Temp., °C	Time, h	% Conv.	$\overline{M}n \times 10^{-3}$	$\overline{M}w \times 10^{-3}$	$\overline{M}w/\overline{M}n$
1	36 (0.346)	0.015 (0.06)	0.013 (0.08)	Camphor sulfonic acid (0.018)	127	3	—	107.6	147.4	1.37
2	15 (0.144)	0.15 (0.06)	0.22^a (1.2)	—	145	3.5	—	11.7	14.3	1.22
3	12 (0.115)	—	0.10 (0.64)	—	130	39	32	1.66	4.29	2.58
4	12 (0.115)	—	0.10 (0.64)	Benzoic acid 0.08 (0.66)	130	39	58	7.30	10.33	1.41
5	12 (0.115)	—	0.10 (0.64)	Camphor sulfonic acid 0.076 (0.32)	130	39	48	9.6	15.5	1.61
6	12 (0.115)	—	0.30 (1.9)	—	120	~24	~80	—	—	1.3

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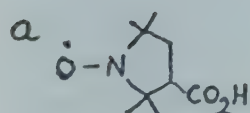
A similar initiator system was also reported to be effective for the controlled polymerization of vinyl acetate[25]. A 1:1:2 complex of aluminum triisobutyl, 2,2′-bipyridyl and TEMPO was polymerized in benzene at 20 to 60°C for 12-24 h. The reaction was first order in monomer as shown by the linear time - conversion plot. Thus, the monomer is involved in the rate limiting step and indicates a constant concentration of active species. $\overline{M}n$ also increased linearly with time. These observations indicate that the initiation is rapid and transfer/termination reaction is minimal. From the kinetic data, the order with respect to initiator was found to be 0.3. The apparent activation energies were found be 6.7 kcal mol^{-1} which is higher than that for the free radical polymerization of vinyl acetate ($Ea = 4.5$ kcal mol^{-1}). The higher activation energy could be due to the combined contribution of activation energy for radical propagation and the enthalpy of the equilibrium between the active and the dormant species. The polymerization rate was strongly accelerated in the presence of two equivalents of TEMPO. At four equivalents, the reaction was completely inhibited. Using a vinyl acetate concentration of 2.5 M in benzene and a Al (iBu)$_3$-2,2-bipyridine-TEMPO (1:1:2) and initiator concentration of 0.05 M or 0.3 M at 20 or 60°C resulted in a polymer with $\overline{M}w/\overline{M}n < 1.3$ with marginal broadening of distribution with increasing conversion. $\overline{M}n$ up to 30,000 could be obtained.

These observations were rationalized based on a hexacoordinated aluminum bound to the bipy ligand and two molecules of TEMPO (dormant species) which is in equilibrium with an alkyl radical (active species) and a penta coordinated aluminum compound[25]. However, the $\overline{M}n$ vs per cent conversion plot and ln $[M]_0/[M]$ vs time plot showed significant curvature, indicating that the concentration of active center was not constant throughout the reaction period. In the case of MMA, severe transfer reactions were observed. Polydispersity values were not reported. The limitation of stable free radical mediated

polymerization has been discussed[26]. Without providing experimental details, it is claimed that homopolymers of *n*- butylacrylate ($\overline{M}n \sim 15,000$, $\overline{M}w/\overline{M}n = 1.5$) and poly(styrene) ($\overline{M}n \sim 200,000$ and $\overline{M}w/\overline{M}n = 1.3$) as well as random block copolymers of styrene and *n*- butylacrylate (65% conversion, $\overline{M}n \sim 25,000$ and $\overline{M}w/\overline{M}n = 1.5$) can be prepared using nitroxide mediated polymerization.

The behaviour of stable free radical mediated controlled radical polymerization can be best understood based on a mechanism, involving fast initiation by radicals generated by TEMPO assisted decomposition of radical initiator followed by reversible trapping of the polystyryl radical by scavenging TEMPO to form dormant alkoxyamines. Alkoxyamines are thermally unstable at temperature > 120°C and can reversibly decompose, generating polystyryl radical and releasing TEMPO. Thus, irreversible termination by radical coupling is minimized. Because radicals are continuously generated, they will also react with the dormant alkoxyamines in a degenerative transfer process. The active and the dormant species exchange rapidly, resulting in linear growth of all chains with conversion and leading to polymers with narrow polydispersities (Scheme 2). The polydispersity in the bulk living free radical polymerization mediated by nitroxide is controlled by the exchange rate between the growing and dormant chains[27].

The TEMPO molecule attached to chain ends is extremely stable and is resistant to hydrolysis under all conventional polymer termination conditions. Even alkali treatment cannot hydrolyze the carbon-TEMPO bond! The only method currently available to eliminate the TEMPO molecule from the polymer chain end is by reaction of the polymer with a large excess of tri-n-butyltin hydride.

Reversible Complexation of Radicals with Organometallic Compounds

Carbon based radicals exhibit reversible complexation behaviour with several organo metallic compounds. Such complexes play an important role in biological systems as well as in synthetic organic chemistry for the formation of carbon - carbon bonds. Metal mediated radical reactions can promote many C-C bond forming reactions in organic chemistry with a high degree of regio - and stereoselectivity[28]. It is therefore not surprising that polymer chemists
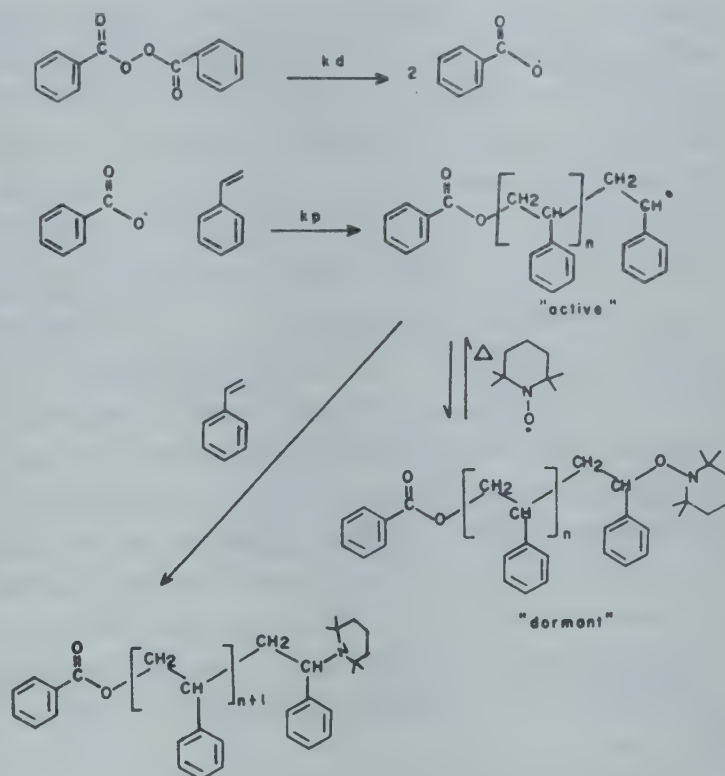
Scheme 2 — Mechanism of styrene polymerization initiated by BPO in the presence of TEMPO

have attempted to exploit the potential of this method for controlled synthesis of polymers.

Aromatic diazonium salts decompose in the presence of metal complexes to yield radicals which initiate the polymerization of MMA with a reasonable degree of control using 5 *M* MMA in THF - acetone (1:1) at 40°C, various metal acetates (Ce, Co, Cr, Rh) were found to initiate polymerization using *p*- chlorobenzene diazonium tetraborofluorate. Ce (OAc)$_2$ gave the best results. The maximum $\overline{M}n$ that could be obtained was 30,000 after 6 h[29]. The polydispersity index was in the range of 1.5 - 1.8 in the conversion range of 20-80%. The polymer had a syndiotacticity of 65-70% as expected for conventional free radical polymerization. Under similar conditions, methyl acrylate gave uncontrolled polymerization.

Kato *et al.*[30] have recently reported that the Kharasch reaction can be used to initiate the controlled polymerization of MMA. The Kharasch reaction involves the addition of CCl$_4$ to an unsaturated double bond, giving the 1:1 adduct in high selectivity and yields. The reaction proceeds by a radical mechanism in which the transient radical is confined in the coordination sphere of a transition metal atom and thus remains stabilized. Many metals have been used for the promotion of Kharasch reaction . If the Kharasch

reaction can be induced to occur successively with additional monomer, then polymerization would occur. However, using conditions under which CCl₄ can be activated, C-Cl bond cannot be activated. However, in presence of a Lewis acid, methylaluminum bis-2,6-di-t-butyl phenoxide, [Me Al (ODBP)₂] at 60°C, 90% conversion was obtained in 4 h. The resulting PMMA had $\overline{M}n \sim 5200$ and polydispersity index of ~ 1.3. No polymerization was observed in the absence of either Ru or Al compound. The semilogarithmic plot of $\ln([Mo]/[M])$ vs time was linear indicating that the reaction was first order in monomer. The plot of $\overline{M}n$ vs conversion deviated from linearity beyond 25% conversion and became progressively lower than $\overline{M}n$ calculated, indicating the presence of distinct transfer reactions. Monomer resumption experiment indicated that the chain ends were quasi living in nature.

A free radical mechanism was inferred from these and other results. The proposed pathway involves an equilibrium between Cl terminated PMMA chain end (dormant) and a PMMA radical stabilized by the coordination with the ruthenium atom. The role of the Lewis acid is to coordinate with the carbonyl group of the ester end thus activates the tertiary — C-Cl bond for homolysis by Ru[II] (Scheme 3).

Instead of CCl₄, α-halocarbonyl compounds can be employed[31]. Examples are 1,1,1-trichloroacetone, α, α-dichloroacetophenone and ethyl-2-bromoisobutyrate. Aluminum isopropoxide was found to be the best Lewis acid. Polymerization of MMA was conducted at 80°C in toluene using [MMA]₀ = 2.0 M, [α-halocarbonyl compound]₀ = 20 mM, [RuCl₂(PPh₃)₃]₀ = 10 mM, [Al(OiPr)₃]₀ = 40 mM. The time to reach 50% conversion was about 9 h for ethyl 2- bromo- isobutyrate, 14 h for α, α- dichloroacetophenone and 16 h for 1,1,1-trichloroacetone. The polymerization showed familiar features of a living polymerization, namely constant concentration of growing species with time, $\overline{M}w/\overline{M}n < 1.2$, linear increase of $\overline{M}n$ with time and resumption of polymerization by addition of fresh monomer, resulting in increase in $\overline{M}n$, in direct proportion to monomer conversion and in good agreement with the calculated values. Furthermore, when using the α, α-dichloroacetophenone as initiator, quantitative incorporation of phenyl group into the polymer was demonstrated. The number average end functionality of the initiator moiety (phenyl group) was 1.01, indicating that an α-halocarbonyl compounds in fact serve as an initiator that forms one living poly(MMA) chain per molecule. Results with Ru[II] catalyzed MMA polymerization are summarized in Table 2.

The above reaction, thus involves the reversible activation of a C-Cl bond, at the growing end of the reaction. It thus bears a striking mechanistic resemblance to the living cationic polymerization of isobutylvinyl ether with HCl/ZnCl₂ and isobutylene/styrene with cumyl chloride/BCl₃ or TiCl₄ systems.

Cobaloximes and Co-porphyrins react reversibly with primary and secondary alkyl radicals. Thus, they are useful initiators for the polymerization of acrylates. Harwood and coworkers[32] have shown that a bisoxime complex of Co[III] photopolymerizes ethyl acrylate in chloroform at 25°C. 100% conversion could be obtained in 5 h. Various diagnostic tests were performed to show the living character of the chain end. These are: the absence of Tromsdorff effect, linear relationship between $\overline{M}n$ vs conversion and ability to functionalize the chain ends. Although the feasibility of polymerizing both acrylonitrile and vinyl acetate as well as block copolymer synthesis by sequential monomer addition were mentioned, no experimental results were provided. A (tetramethyl porphyrinato) cobalt neopentyl has been shown to initiate the living free radical polymerization of acrylates[33]. Using methyl acrylate[33] (2.5 M in benzene)
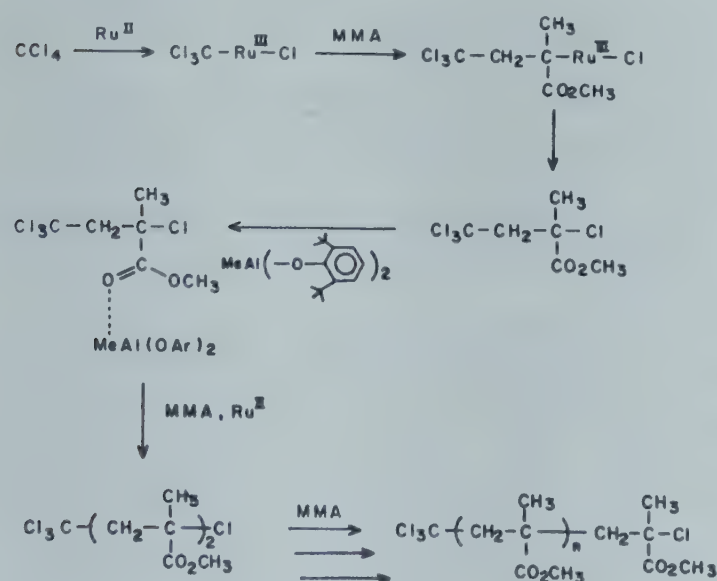
Scheme 3 — Mechanism of methyl methacrylate polymerization initiated by Ru[II]

Table 2 — Polymerization of methyl methacrylate using Ru^{II} / halo compounds/Lewis acids

[MMA] M	[RuCl$_2$ (PPh$_3$)$_3$] mM	Lewis acid mM	Halogen Cpd., mM	Temp, °C	Time, h	Conv.%	$\overline{M}n \times 10^{-3}$	$\overline{M}w/\overline{M}n$
2.0[a]	10	40[b]	20[c]	60	4	90	5.2	1.32
2.0[d]	10	40[e]	20[f]	80	60—80	90	10.4	1.15

[a] in n-heptane (2.5 mL), [b]Methylaluminiumbis(2,6—di—tert—butylphenoxide),[c]CCl$_4$
[d]in toluene (2.5 mL), [e]Aluminium isopropoxide, [f] α,α,—dichloroacetophenone
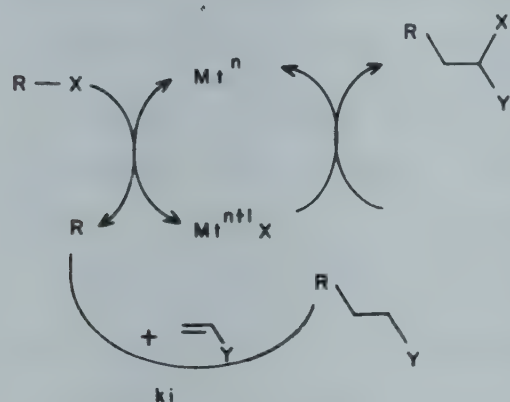
Scheme 4 — Atom transfer radical addition reaction

Scheme 5 — Atom transfer radical polymerization reaction

and (TMP) Co-CH$_2$-C(CH$_3$)$_2$ (1 x 10^{-3} M), at 60°C, resulted in a polymer (70% conversion, $\overline{M}w/\overline{M}n$ = 1.21). The plot of $\overline{M}n$ vs conversion was linear till about 70 to 80% conversion. The living nature of chain end was demonstrated by the synthesis of a methyl acrylate - butyl acrylate copolymer by sequential monomer addition ($\overline{M}n$ (MA-b-BA) 131,400, $\overline{M}w/\overline{M}n$ = 1.29).

Atom Ttransfer Rradical Ppolymerization (ATRP)

Atom transfer radical addition (ATRA) is a well known method for C-C bond formation in organic synthesis[34]. ATRA is also promoted by transition metal catalysts[28]. In these reactions, catalytic amount of transition metal compound act as a carrier of the halogen atom in a redox process (Scheme 4). The high efficiency of metal catalyzed ATRA suggests that the presence of M_{tn}/M_{tn} H redox process provides a low concentration of free radicals resulting in reduced termination reaction between radicals.

The concept of ATRA has been extended to polymerization (atom transfer radical polymerization ATRP) (Scheme 5) of styrene and methyl methacrylate[35]. An alkyl chloride, namely 1-phenyl ethylchlo-

ride, is an efficient initiator and a transition metal halide CuCl, complexed with 2,2'-bipyridine, an efficient chlorine atom transfer promoter. For styrene polymerization at 130°C, $\overline{M}n$ increased linearly with conversion. Furthermore, the polymerization was first order in monomer concentration and $\overline{M}w/\overline{M}n$ was in the range of 1.3-1.45. These results suggest a living polymerization process with a negligible amount of irreversible transfer and termination. In the absence of 1- phenylethyl chloride, CuCl or 2,2'-bipyridine, polymers with broad molecular weights distribution and ill- controlled molecular weight were obtained. The method is general and works well with both styrenic and acrylic monomers (Table 3). The end group analysis of poly(methyl acrylate) initiated by 1- phenylethyl chloride by NMR confirms the mechanism (Scheme 5). The polymer has an Ar-CH- CH$_3$ group at the head and a chlorine atom at the tail.

Table 3 — Atom transfer radical polymerization initiated with RX/CuX/2,2'—bipyridine[a]

Monomer	RX/CuX	Temp., °C	$\overline{M}n$(theory)	$\overline{M}n$ (SEC)	$\overline{M}w/\overline{M}n$
Styrene	1-Phenylethyl chloride/CuCl	130	120, 000	110, 500	1.45
	1-Phenylethyl bromide/CuBr	100	97, 000	93, 300	1.50
	1-Phenylethyl bromide/CuBr	80	8, 300	8, 000	1.25
Methyl acrylate	Ethyl 2-chloropropionate/ CuCl	130	30, 500	31, 000	1.40
	Ethyl 2-bromopropionate/ CuBr	80	19, 100	21, 500	1.25
	Methyl 2-bromopropionate/ CuBr	100	27, 500	29, 100	1.14
Butyl acrylate	Methyl 2-bromopropionate/ CuBr	130	15, 000	13, 500	1.50
Methyl[a] methacrylate	Ethyl 2-bromoisobutyrate/ CuBr	100	10, 000	9, 800	1.40

[a]Molar ratio of RX/CuX/2,2-bipyridine= 1:1:3, [b] In ethylacetate, 50% by volume

ATRP can also be initiated using conventional radical initiators, e.g. AIBN, instead of 1-phenylethyl halides[36]. In these cases, large excess of Cu(II)Cl$_2$ and 2,2'-bipyridine are required. Typically, polymerization of styrene at 130°C, using ten-fold molar excess of Cu^{II} Cl$_2$ and twenty-fold molar excess of 2,2'-bypyridine results in well controlled polymerization with 95% I$_{eff}$ and $\overline{M}w/\overline{M}n$ ~ 1.30. The higher molar excess requirement of Cu^{II} Cl$_2$ was presumably due to its poor solubility in the system. Cu^{II} Cl$_2$ is known to be an efficient and strong inhibitor/retarder of radical polymerization. However, at high temperatures and in the presence of a coordinative ligand such as bipyridine, a reversible activation of the polymeric alkyl chloride occurs.

Under identical conditions, methyl acrylate failed to undergo controlled polymerization. However, use of 2-chloropropionitrile as a coinitiator along with Cu^{II} Cl$_2$ and 2,2'- bipyridine and 1 mol% AIBN relative to 2-chloropropionitrile resulted in controlled polymerization of methyl acrylate.

ATRP can also be initiated by other reactive halides. Recently, Percec and Barboiu[34] have shown that arenesulfonyl chloride in the presence of Cu^I Cl and 2,2'-bipyridine initiates the bulk polymerization of styrene[37]. Good molecular weight control was obtained. The polydispersities were in the range of 1.50 - 1.80. Both arylsulfonyl and chlorine groups were detected at the terminal end of the polymer.

One of the disadvantages of the Cu^I/Cu^{II} alkyl halide or arenesulfonyl halide systems is that they are heterogeneous. 2,2'-Bipyridine only partially solubilizes the catalyst system. This limits the complete monomer conversions using the above catalysts. It has been found that 4,4'-dinonyl- 2,2'-bipyridine forms a very soluble complex with Cu^I Cl and can be used for the homogeneous polymerization[38]. Use of homogeneous catalysts improves the molecular weight distribution (1.30 vs 1.4 for heterogeneous catalysts). Recently, the kinetic features of ATRP of methyl acrylate and styrene have been elucidated[39].

ATRP, thus, is a simple, inexpensive and general method for controlled radical polymerization of styrene and acrylate monomers. The presence of a cata-

lytic amount of growing radicals and fast equilibration between growing radicals and dormant species are essential for successful atom transfer radical polymerization. Under well-defined conditions, ATRP can produce poly(styrene) with $\overline{M}w/\overline{M}n = 1.05$ ($\overline{M}n = 8{,}777$ and conversion = 78%)[40].

Synthesis of Polymers with Controlled Structures/Architectures Using Living Radical Polymerization

The availability of controlled methods for polymerization opens the doors for new polymer synthesis. It is, therefore, not surprising that availability of efficient methods for controlled radical polymerization has stimulated renewed interest in this area. Novel strategies have been explored for the synthesis of end functionalized polymers[41,42], graft and star polymers[42,43], hyperbranched polymers[44-46], random and block copolymers[47,48]. Using nitroxide mediated stable free radical polymerization block copolymers of poly(styrene) and t-butylacrylate and 4-vinylpyridine have been synthesized. Triblock copolymers of poly(styrene) - poly(isoprene) - poly(styrene) were prepared by sequential monomer addition[49].

Functionalized unimolecular initiators derived from monoadducts of benzoyl peroxide, styrene and TEMPO were prepared (Scheme 6). Using these functionalized initiators, hydroxy and amino end functionalized poly(styrene)s were prepared[41]. Possibilities of synthesizing functionalized polymers using ATRP have been pointed out[42]. Use of initiators such as Y-R-X, where Y = -CO$_2$H, -OH, -CN, C=C, naphthyl and X = Cl, Br, should yield polymers with end functionalization Y. Block copolymers of methyl acrylate with styrene by ATRP has been reported[42]. Polymerization of methyl acrylate by 1-phenylethyl chloride/Cu^I Cl/bipyridyl at 130°, resulted in a poly(methyl acrylate) with a terminal chlorine end group. Addition of styrene and further polymerization resulted in a block copolymer, poly[(methyl acrylate)-b-styrene]. The $\overline{M}n$ of polymethyl acrylate) block was 2080 ($\overline{M}w/\overline{M}n = 1.25$), whereas that of the poly(styrene) block was 6240 ($\overline{M}w/\overline{M}n = 1.35$). ATRP has been applied to homopolymerization of acrylonitrile and its block copolymerization with n-butylacrylate and 2-ethylhexylacrylate[50].
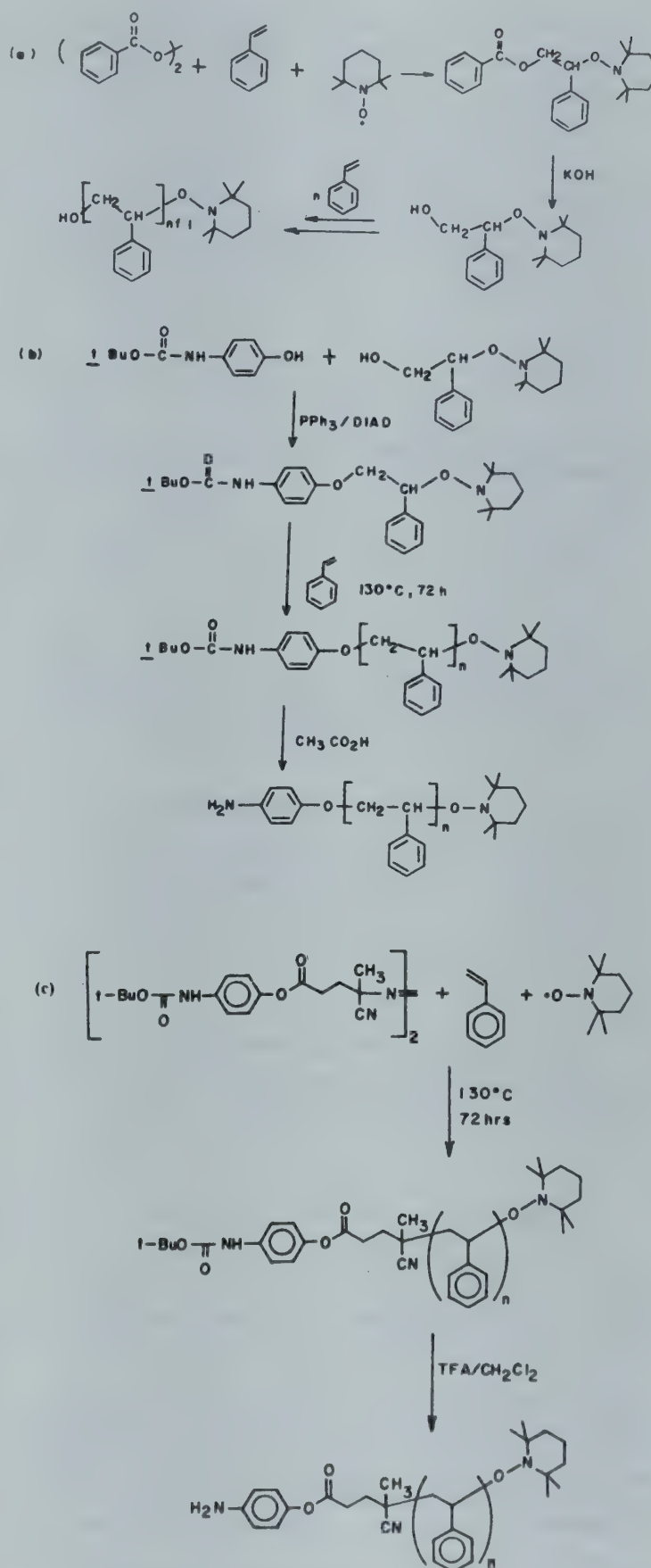
Scheme 6 — End functionalized polymers by stable free radical mediated polymerization

Star shaped polymers have been successfully synthesized using both stable free radicals mediated and atom transfer radical polymerizations (Scheme 7).

(a)

(b)

1   2   6

$$\overline{M}n \; SEC = 62400, \; \overline{M}n \; _{theory} = 60,000$$

$$\overline{M}w \, / \, \overline{M}n = 1.23$$
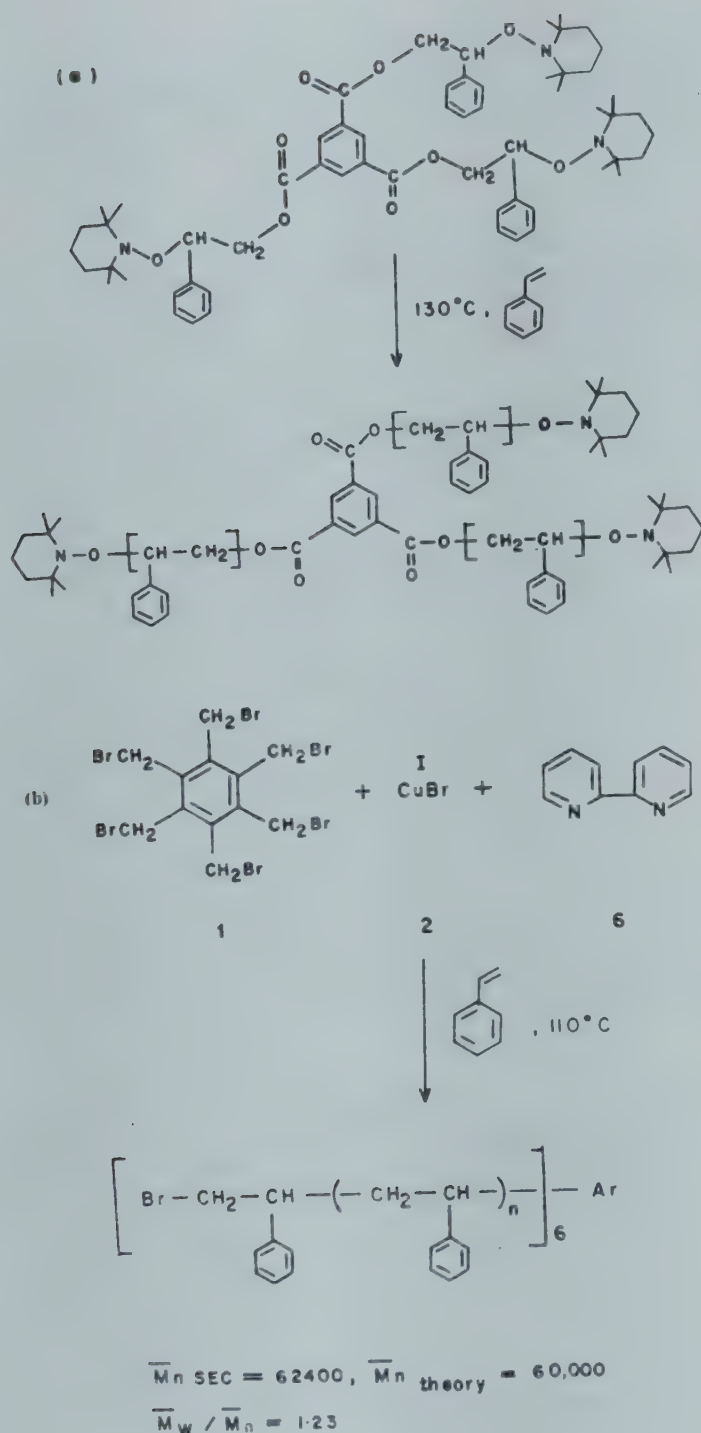
Scheme 7 — Branched polymers using living free radical
polymerizations

Three-arm poly(styrene)s and six arm poly(sty-
rene)s, poly(methyl acrylate)s and poly(methyl
methacrylate)s have been synthesized[42,43]. Three arm
poly(styrene)s with arm molecular weights $\overline{M}n$
(SEC) = 22,000, $\overline{M}n$ (theory) = 24,000 and $\overline{M}w/\overline{M}n$
= 1.09 were prepared in 88% yield. The interesting
feature of the six=arm polymers prepared by ATRP
is that every arm contains a halogen terminal group,
capable of being further functionalized (Scheme 7b).
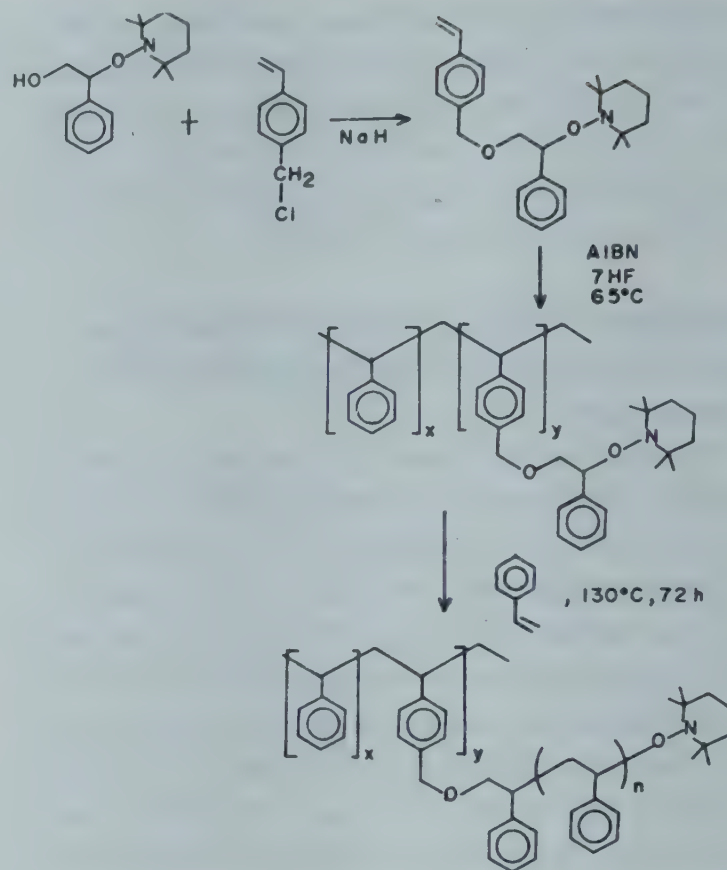
Scheme 8 — Graft copolymerization of styrene using living
free radical polymerization

Graft copolymers have also been prepared using
living free radical polymerization techniques
(Scheme 8). Random copolymers of styrene with
methyl methacrylate or *n*-butyl acrylate have been
synthesized (Scheme 9). Traditional methods such as
anionic, cationic or group transfer polymerization
techniques are not suitable for the synthesis of ran-
dom copolymers from disparate vinyl monomers
such as styrene and acrylates. Polymers with a range
of composition, controlled molecular weight and end
functionality and narrow polydispersities (1.1 - 1.6)
have been reported.

Recently, Frechet and coworkers[44] have proposed
a new class of vinyl polymerization, namely, self-
condensing vinyl polymerization, which promises to
be a simple method for the synthesis of complexed
branched polymer structures (Scheme 10). This prin-
ciple has been applied to controlled and living radical
polymerization of suitable[45,46] precursor monomers
(Scheme 11) to yield hyperbranched polysty-
renes[45,46].

$\overline{M}_n$: 9000

$\overline{M}_w/\overline{M}_n$: 1·22

Yield : 81%
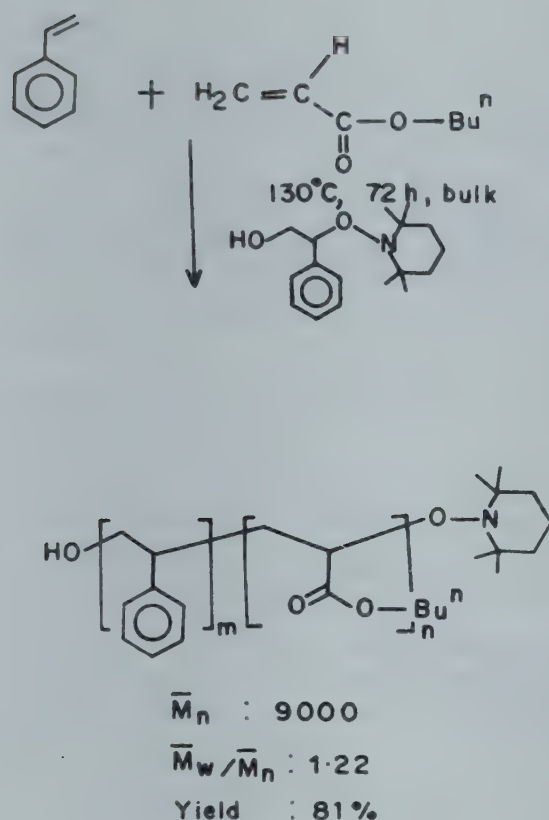
Scheme 9 — Random copolymerization of styrene and butyl acrylate using living free radical polymerization

(Scheme 11) to yield hyperbranched polystyrenes[45,46].

Concluding Remarks

The emergence of the living radical polymerization chemistry capable of producing polymers with controlled molecular weights and narrow molecular weight distributions within the last three years has opened up new horizons in polymer synthesis. In a very short duration, chemists have exploited this technique, creatively, for the synthesis of polymers with well defined architectures and novel functional polymers, previously obtainable only under synthetically more rigorous living anionic or cationic polymerization conditions. More significantly, the emergence of this chemistry, has further unified the mechanistic concepts underlying many of the well known living polymerization processes, namely anionic polymerization of methyl methacrylate, cationic polymerization of styrene, isobutylene and isobutyl vinyl ether and group transfer polymerization of methyl methacrylate[51]. In every case, enhanced livingness with negligible contributions from chain breaking or termination reactions has been achieved by invoking the concept of "reversible ter-
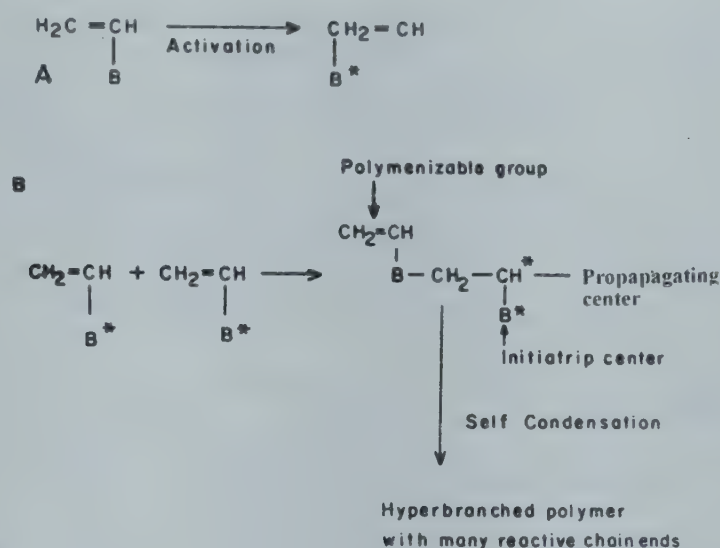
Scheme 10 — Self-condensing vinyl polymerization

mination" involving an "active" species in rapid equilibrium with a dormant species.

Acknowledgement

Abbreviations

AIBN =Azo-bis-isobutyronitrite; BPO =Benzoyl peroxide; $[C^*]$ = Concentration of active species; DPn =Number average degree of polymerization; I_{eff} =Initiator efficiency, defined as the ratio of $\overline{M}_n$, as determined by SEC to $\overline{M}_n$, calculated from $[M]_o$ and $[I]_o; [I_o]$. = Initial initiator concentrations; K_p =Rate constant of propagation; K_t =Rate constant for termination; $\overline{M}_n$ =Number average molecular weight; $[M]_o$ =Initial initiator concentration; $\overline{M}_w$ =Weight average molecular weight; $\overline{M}_w/\overline{M}_n$ =Polydispersity index, ratio of weight average to number average molecular weights; R_p =Overall rate of polymerization; SEC = Size exclusion chromatography; TEMPO =2,2,6,6-tetramethyl-1-piperidinyloxy.
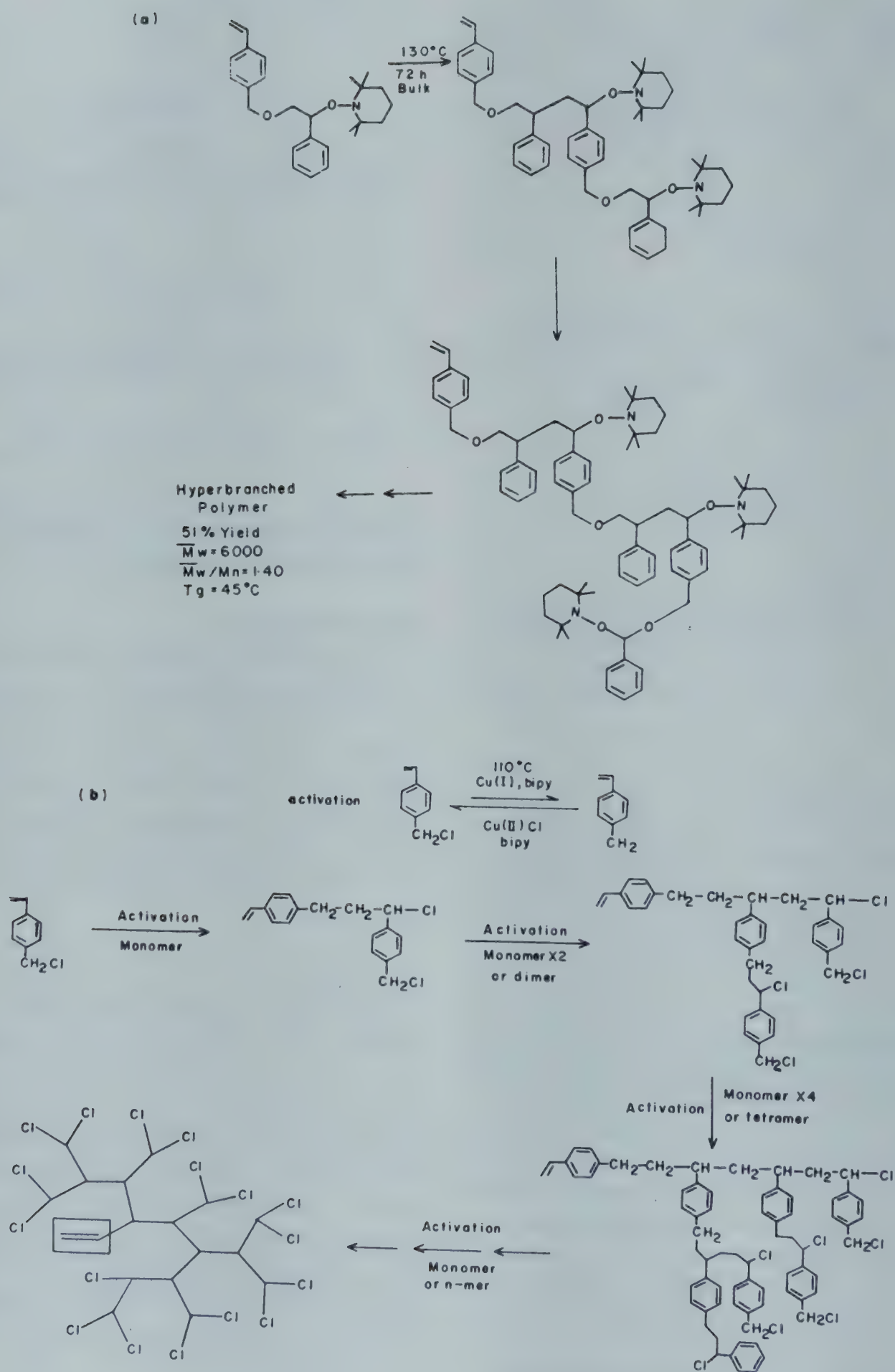
Scheme 11 — Living free radical self-condensing vinyl polymerization approach to hyper-branched poly (styrene)s

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Role of Some Transition Metal Ions in Oxygen-Mediated Toxicity

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Transition metal ions play an important role in the production of radical species. These ions are capable of catalyzing redox reactions between biomolecules and oxygen that would not occur unless catalytically active metal ions were present. The ability of the transition metal ions to move electrons is the basis for the formation and propagation of many of the most toxic radical reactions. In this review attention has been drawn to the metabolism and redox cycling of metal ions in oxidative stress of biological systems, and also during the metabolic interactions of these metal ions and the oxygen-derived free radicals in the pathogenesis of metal ion toxicity.

Introduction

There are now rapidly accumulating evidences which strongly suggest that transition metal ions play an important intermediatory role in oxygen-mediated injuries to biological macromolecule such as lipids, proteins and DNA. If catalytic metal ions are not available, then superoxide radicals and hydrogen peroxide at physiological concentrations may have limited (if any) damaging effects[1]. This principle underlines the importance of examining the availability and distribution of catalytic metal ions in understanding oxidative damage to the cells. Metal ions are involved in the action of many drugs and toxic agents. In some of the cases, metal ions are essential for the expression of the activity of various drugs and toxic agents, while in others, they just enhance the effect, and in some cases, they even provide protection by inhibiting the activity of these compounds. In many systems, where oxy-radicals are involved, transition metal ions or their complexes play a major role in enhancing the damage caused by these radicals[1].

The focus of this review is on the role of various transition metal ions in oxidative stress during the metabolic interaction of metal ions, and the action of oxygen-derived free radicals with biomolecules. Some likely therapeutic avenues in toxicities where these metal ions are involved are also discussed.

Metal-Mediated Activation of Oxygen Species

Molecular oxygen is essential for living organisms, which does not exceed the reactions in chemical and biological systems because of its unique electronic configuration. Although, it is a good oxidant, the quantum mechanic restrictions do not favour the reaction of molecular oxygen with organic compounds. Therefore, dioxygen must be activated for the oxidation of these compounds to occur. Activation can proceed via several processes, among them are the activation to singlet oxygen and reduction by organic radicals. But, the most important mechanism for dioxygen activation in biology involves the formation of its complex and/or reduction by transition metals. The following expressions represent a Fenton-type reaction, where M is Cu(I), Fe(II), Co(II), Ni(II) or Ti(III) aquo cations.

$$M^{n+} + H_2O_2 \rightarrow M^{(n+1)+} + {}^-OH + {}^\cdot OH \qquad \ldots (1)$$

$$M^{(n+1)+} + O_2^{\cdot -} \rightarrow M^{n+} + O_2 \qquad \ldots (2)$$

$$\text{or} \quad M^{n+} + O_2^{\cdot -} + 2H^+ \rightarrow M^{(n+1)+} + H_2O_2 \qquad \ldots (3)$$
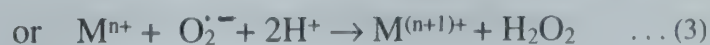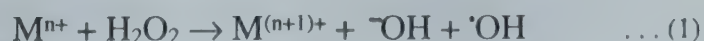
There are peculiar differences between Fe(II) and Co(II) reacting with H_2O_2 in a way that beside forming the $\cdot OH$ radical, Co(II) also catalyzes production of $O_2^{\cdot -}$(ref 2). Combining the reactions (1) and (2),

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which can be driven by aquo cations of Cu(II) and Mn(II), and by some complexes of Cu(II), Fe(II) and Ni(II) but not by Ni(II) aquo cations themselves [3,4]. The major substrates for these reactions are: H_2O_2 and O_2^-, generated in aerobic organisms during oxidative metabolism[5,6]. The same oxygen derivatives may also be produced by some metal aquo cations or complexes directly from ambient oxygen, in autooxidation reaction, e.g.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \qquad \ldots (4)$$

With subsequent production of H_2O_2 according to Eq.(3), various metal compounds interacting with H_2O_2 may produce yet another form of active oxygen, called singlet oxygen $^1O_2$ (refs 7,8). Although, it is the metal cation itself that drives electron transfer, the ligand environment in which the reacting metal is coordinated may have a profound effect on that transfer. Chelation of the cation may either enhance or inhibit the reactions. For example, autooxidation of Fe(II) to Fe(III) is enhanced by ethylenediamine tetraacetic acid (EDTA) or nitrilotriacetic acid (NTA)[9], and inhibited by o-phenanthroline and deferoxamine[10]. In the presence of inorganic ligands, Ni(II) is fully resistant to the attack of O_2 and/or H_2O_2. Oxidation of Ni(II) and its reactivity towards H_2O_2 may, however, be facilitated by chelation with several small peptides or proteins. Likewise, Co(II) aquo cations, which are stable in air, become sensitive to O_2 in the presence of chelators[2]. Quite often, the organic ligand becomes the first target of oxygen activated by coordinated metal cation, and the ligand degradation products may interact with other molecules, including proteins and DNA[11].

Transition Metals

Transition metal ions are important in the production of radical species. The ability of these ions to move electrons is the basis for the formation and propagation of many of the most toxic radical reactions. For example, the superoxide anion is relatively non-reactive in aqueous solutions. However, in the presence of H_2O_2 and a transition metal, the extremely reactive hydroxyl radical may be generated. This pathway, known as iron-catalyzed Heber-Weiss reaction (as described above), is a typical Fenton chemistry, and has been extensively studied.

Although its role in pathology is not well established, the extensive measures taken by cells to minimize the presence of free metal ions, indirectly indicates that such reactions are detrimental to biological systems.

Chromium

Chromium is rapidly taken by the cells as hexavalent chromate via passive anion transport channels, where it is eventually reduced to Cr(III). Generally, under physiological conditions, Cr(VI), in the form of chromates, is non-reactive towards DNA. It is, however, capable of reacting with redox-active enzymes and small molecules to produce Cr(V), Cr(IV) and Cr(III), as well as oxygen- and sulphur-centered radicals. All these species can damage DNA. Hence, the ability of Cr(VI) to damage DNA depends on cellular redox systems. One such system depends on glutathione and produces Cr(V) and sulphur-centered glutathione-ethyl radical[12,13], which may attack DNA. Cr(VI) may also be reduced by a variety of other cellular components, including molecules of mitochondrial electron transport chain, carbohydrates, ascorbic acid and H_2O_2[11,14]. Reduction of Cr(VI) with H_2O_2 leads to the production of $^\bullet OH$. Hydroxyl radical and Cr(V) are also generated when Cr(VI) is reduced enzymatically by glutathione reductase, a ubiquitous cellular enzyme[14]. Further, Cr(V), the first intermediate of the reduction, has been recently found to decompose H_2O_2 and produce $^\bullet OH$ in a Fenton-type reaction[14]. Therefore, it has been proposed that $^\bullet OH$ is the ultimate carcinogenic species in Cr(VI) carcinogenesis[14]. It has also been shown that Cr(VI)- and Cr(V)-GSH-induced DNA damage was inhibited by OH scavengers such as dimethyl sulphoxide, formate, benzoate as well catalase, which degrade H_2O_2 and water.

Nickel

Extensive epidemiological studies have shown that the incidence of occupational respiratory tract cancer is high in those men who are exposed to nickel compounds[15,16]. The Ni-derivatives were shown to induce hepatotoxicity through formation of lipid hydroperoxides[17], which was suppressed by benzoate, an OH scavenger[18]. Recently, more convincing evidence of Ni-mediated generation of reactive oxygen species (ROS) is the formation of many oxidized bases in DNA of cultured human cells exposed to

Ni[19]. It has been shown that Ni(II) ions themselves cause virtually no (or little) damage to the isolated DNA[7,8]. It is noteworthy that in the presence of very low concentration of H_2O_2 in which DNA damage would not occur, Ni(II) causes base alteration(s) and sugar phosphate backbone breakage. The possibility that Ni(II) plus H_2O_2 causes DNA damage *in vivo* is supported by the fact that a considerable amount of H_2O_2 is generated in nuclei[20]. It has been further reported that DNA damage is induced by H_2O_2 through the Fenton reaction under both *in vivo* and *in vitro* conditions[5,6,21].

Cobalt

Cobalt is thought to be a carcinogenic metal[22]. The genotoxic effects of cobalt salts in human and animal cell cultures and their carcinogenicity in humans and animals have been reviewed[23] recently. The production of a number of other biological dysfunctions by cobalt compounds *in vitro* and *in vivo* was reported[24] by Robinson *et al.*[24]. The mechanisms underlying cobalt toxicity have not been worked out, but it is hypothesized that the oxygen-derived species may be involved[25-27]. It has been proposed that oxidation of some organic compounds by cobalt complexes in the presence of alkyl hydroperoxides, oxygen or hydroperoxide is involved through oxygen-centered free radicals, which proceeds via a Haber-Weiss mechanism[28,29]. It has been suggested that Co(II) reacts with H_2O_2 to form $^{\cdot}OH$[29], but this view has been questioned on the basis of electron spin resonance studies[30]. Recently, it has been shown that Co(II) ions in the presence of H_2O_2 cause chemical changes in DNA bases in chromatin, extracted from cultured cells of human origin[19]. Several modified DNA bases in chromatin were identified and these products were typical hydroxyl radical-induced DNA bases, suggesting that hydroxy radical is involved in their formation. This idea was supported further by the partial inhibition of product by typical scavengers of hydroxyl radical. Hydroxyl radical-induced products of DNA bases were identified in cultured cells of human origin[19]. These findings suggest that DNA damage in chromatin-mediated by Co(II) ion in the presence of H_2O_2 may contribute to the established genotoxicity and carcinogenicity of cobalt ions.

Cadmium

The genotoxic potential of cadmium has been well-established using *in vitro* systems[31,32]. Cadmium has been shown to induce DNA damage in cultured cells, and the available evidences suggest that this DNA damage is the result of free radical generation[33,34]. Ochi *et al.*[35] demonstrated the ability of cadmium chloride to induce single-strand DNA damage in cultured Chinese hamster V-79 cells under aerobic conditions. However, under anaerobic conditions, cadmium was unable to induce DNA strand damage. In addition, superoxide dismutase was found to reduce greatly the genotoxicity associated with cadmium exposure. These results indicate the involvement of active oxygen species in cadmium-induced DNA strand breaks. Further studies from their laboratory provided evidence of a peroxidant state induced by cadmium chloride. These studies have also demonstrated the ability of butylated hydroxytoluene (BHT), a diffusible radical scavenger, to suppress cadmium-induced inhibition of cell growth, thymidine incorporation into the acid-soluble fraction of cells and metal-induced clastogenecity. In addition, mannitol (a hydroxyl radical scavenger) was able to suppress cadmium-induced inhibition of cell growth and thymidine incorporation. Although, cadmium treatment had no effect on superoxide dismutase, catalase, glutathione peroxidase or reductase levels were reduced within these cells, which may be responsible for the role of active oxygen in the toxicity and clastogenecity associated with cadmium exposure.

Copper

Copper is an essential trace element in all species[36]. The majority of well-characterized copper metalloenzymes catalyze oxidation-reduction reactions. The biochemical basis of copper toxicosis is not clear and is presumably multifaceted. Excessive tissue copper concentrations may affect the stability of membrane, cellular redox state, synthesis and function of proteins, and replication and transcription of DNA[37,38]. Some of the deleterious effects may be mediated by the highly reactive hydroxyl radicals. Cuprous ions can catalyze formation of hydroxyl radicals in a reaction of superoxide anions and hydrogen peroxide[39], which are capable of causing scission in DNA[40,41]. Both, superoxide anion and

hydrogen peroxide, are present in cells undergoing normal oxidative metabolism.

Iron

The most abundant transition metal in biological systems is iron, and literature shows that it is a potent catalyst of oxidative stress. Iron plays a central role in several aspects of free-radical-mediated toxicities and pathologies associated with oxidation of biological macromolecules. It can exist in several oxidation states[42,43]. The importance of iron in mediating oxidative damage naturally leads to the question as to what forms of iron might be available to catalyze radical reactions *in vivo*. When the idea that toxicity of superoxide radical and hydrogen peroxide involves hydroxyl radicals was first being formulated[44-46], a debate was going on simultaneously about the availability of catalytic metal ions *in vivo*, with several investigators being dubious about their existence[47]. The picture is now much clearer. Organisms take great care in the handling of iron[48,49] using both transport (transferrin) and storage (ferritin and hemosiderin) proteins so as to minimize the amount of free iron within the cells and also in the extracellular fluids. And thus, this sequestration of transition metals may be regarded as an important contribution to antioxidant defenses[50]. However, oxidative stress can itself provide iron for free radical reactions[50].

Defences against Oxygen Species Derived Damage

The *in vivo* multiple defense system operates against uncontrolled oxidative reactions[51] which could be initiated by $O_2^{\cdot-}$ driven Fenton reactions. Therefore, formation of $O_2^{\cdot-}$, H_2O_2, $^{\cdot}OH$, higher valence states of the metal, or activated complexes should be blocked at any stage, or the system must know how to repair the damage that is caused by these species. In the cells, there are enzymatic and non-enzymatic defenses and one can administer synthetic compounds to the organism, which may protect or diminish the damage.

(a) Enzymatic Defenses

Several enzymes and non-enzymatic antioxidants have been evolved whose primary function appears to be to decrease the amount of oxidant or potential oxidant in the cell, and therefore, to serve a protective function with respect to biological oxidants. The

following are the enzymatic and non-enzymatic defenses:

1. *Superoxide dismutase (SOD)*: This enzyme, discovered by McCord and Day[46], is a metalloenzyme that catalyze O_2^- dismutation into H_2O_2 plus O_2. This enzyme is present at 10^{-5} M concentrations in most aerobic cells. The removal of $O_2^{\cdot-}$ by SOD may provide complete protection since the dismutation of O_2^- produces H_2O_2.

If reduced transition metals are present, the removal of H_2O_2 as well as $O_2^{\cdot-}$ is essential to provide full protection to the cell.

2. *Catalase and peroxidase*: H_2O_2 is produced by the dismutation of $O_2^{\cdot-}$ as well as by a number of oxidases[52]. Accumulation of H_2O_2 can be prevented by catalases and peroxidases, which are heme proteins. Catalase dismutases H_2O_2 into H_2O and oxygen, while peroxidase catalyzes the reduction of H_2O_2 to water. Catalase is present in virtually all mammals, and the intracellular H_2O_2 is strictly controlled by this[52].

(b) Non-enzymatic Defenses

In addition to enzymatic defense against oxidative damage *in vivo*, there are non-enzymatic defenses against these toxicities. While the enzymes remove the initiating species causing the biological damage, the non-enzymatic defenses are provided mainly by antioxidants, and wherein they help terminate free radical chain reactions. The antioxidants, which are lipid-soluble vitamins such as α-tocopherol, β-carotene, and retinoic acid or ubiquinone, act as scavengers of reactive oxygen species, and prevent lipid peroxidation and peroxidative damage.

Effective $^{\cdot}OH$ scavengers such as urate or mannitol, which may protect some of the systems *in vitro*, may also do so in some cases *in vivo*, although it is difficult to distribute them homogeneously in the media, and to reach sufficient concentrations to compete efficiently with the targets in the cell.

In addition, it is possible to block the action of metals in systems where they enhance the damage or to repair the damage once it occurs. As the damage is generally the oxidative damage, very often initially free radicals are formed via hydrogen abstraction, and low concentrations of thiols are capable of reconstituting the molecule via hydrogen donation.

Metal chelators, which irreversibly remove a metal ion from redox cycling, which removes iron effectively and irreversibly, in systems where iron catalyzes oxy-radical damage, e.g. thalassanemia, rheumatoid arthritis, muscular dystrophy, and post-ischemic injury[53]. Similarly, copper overload in Wilson's disease is treated with copper chelator, D-penicillamine, which is very successful in expanding the lifespan of patients with this syndrome[54].

Conclusions and Futuristic Studies

It is now becoming increasingly apparent that numerous pathophysiological phenomena may be related to the transition metals and oxidative damage. The metals' effect(s) may be *direct* (due to metal-binding-related conformational and functional distortions of biomolecules) or *indirect* (due to a variety of structural modifications of biomolecules by metal catalysis- activated oxygen species). For uptake- and toxicity-related reasons, the catalytic effect of metals seems to be rather more important for carcinogenesis than the direct effects.

Further, because the role of transition metals in studies involving biomolecular oxidation has often been overlooked, a strong emphasis of current thoughts to the source, its biological form, and mechanism of action of the biologically active metal species, are presented here. Since the transition metals are involved in the very early stage of reaction leading to oxygen-associated toxicities, further investigations are required to look at the biological aspects of basic transition metal metabolism, which would certainly aid to the development of effective antioxidant drug designs to prevent oxygen-mediated toxicities before they have a chance to begin.

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A New Approach For Measuring Core Electrical Resistivity

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An experimental study to investigate the infuence of variations in test conditions and laboratory procedures on the electrical properties of rocks is presented. Improvements in instrumentation, using a 4-terminal system, and sample-components assembly have been introduced to study the electrical properties of unconsolidated and friable sands in the Niger Delta. Results indicate better electrical resolutions of the 4-terminal electrode than the 2-terminal electrode used at present. Unlike the 2-electrode, the 4-electrode system is not sensitive to voltage frequency and reduces end-face effect. Reliable measurements of cementation and saturation exponents are important in accurate reserve estimation.

Introduction

Electrical resistivity measurements are widely used in well logging and laboratory studies to estimate porosity, water saturation, formation resistivity factor and resistivity index. Solid materials of porous rocks, with the exception of certain clay minerals, are non-conductors of electricity.[1] To improve the reliability of electrical resistivity measurements, the influence of operating conditions must be understood. Many investigators have studied the effect of confirming pressure on cementation factor, especially in sandstone rocks. Except for Redmond[2], they concluded that the increase in m (and f) (see nomenclature at the end for the explanation of variables used) with an increase in pressure is much greater than the corresponding degree in porosity. This conclusion simply means that m is a function of pressure even after porosity correction. The increase is generally attributed to the change in pore structure. However, the adequacy of simulating reservoir conditions in laboratory measurements of electrical resistivity has been questioned for certain complex situations.[3] Research into the effect of changes in confining pressure on saturation exponent, n has been sparsely reported. Performing experiments in sandstone and carbonate rocks, Longeron *et al.*[4] found that n increases or decreases with an increase in confining pressure, depending on rock type. In 1968, Waxman and Thomas[5] showed that large changes in m and n with changes in temperature are only caused by the presence of conductive clays. For clean sands, n is decreased only about 0.05 to 0.10 units with a temperature change from 77 to 176°F.

Two empirical equations developed by Archie[6] form the basis for calculations of reservoir parameters from laboratory-measured values of m and n:

$$F = R_o/R_w = 1/\phi^m \qquad \ldots \qquad (1)$$
$$I = R_t/R_o = 1/S_w^n \qquad \ldots \qquad (2)$$

In the Core Laboratory at the University of Port Harcourt, the procedures for imeasuring electrical properties have been modified to meet the following objectives :

1. Non-damaging sample mounting process
2. Oil-brine capillary drainage at confining stress by the porous disk method for P_c (Capillary pressure) and I versus S_w
3. Electrical properties (F, m and n) at confining stress by the 4-terminal method, including wide spacing of potential electrodes
4. Determining K_{air} and porosity at confining stress before and after test process
5. Facility to hold long samples (up to 3-in) to maximize pore volume, V_p
6. Facility to determine final S_w by Dean-Stark method.

As opposed to earlier 2-terminal method, a 4-electrode method was employed and results compared with the conventional method. The tests simulated downhole pressure on a variety of cores from the Niger Delta. Variations of typical field operating conditions and laboratory procedures were tested for the response of electrical properties. Convenient procedures are described from test results to handle both consolidated and unconsolidated cores to achieve representative properties.. The results obtained corroborated the

findings of Dacy et al.[7] for consolidated formations. The Viton sleeve used by Dacy et al. for 4-electrode electrical property determination is not suitable for many unconsolidated or friable core samples encountered in the Niger Delta. When the Viton sleeve is used for unconsolidated samples, two things could happen due to the rigid nature of the sleeve wall: (1) the core sample may suffer physical damage and (2) the sleeve may fail.

Experimental Procedure

Sample and Fluid Preparation

Plug samples, each 1.5-in. OD and up to 3-in. long were cut and trimmed, using liquid nitrogen as the coolant. Initial mounting materials including a tin sleeve and stainless steel screens were applied to each sample. Weights of mounting materials were recorded and screen pore volumes are known, to make appropriate corrections to pore volumes, length, diameter, etc. While frozen, the samples were individually loaded in hydrostatic core cells and pressured to 1000 psig. These samples were allowed to thaw at that stress value. Following this initial mounting and seating process, the samples were unloaded and individually wrapped in plastic film and aluminium foil and retained in a freezer.

Distilled water was used to simulate the brine according to water analysis. The brine was filtered through 0.45μ Whatman filter paper to remove particles that could block sample pore-spaces before injecting to a core sample. Isopar-L refined oil viscosity 1.5 cP, was used as the non-wetting phase. The oil was degased and filtered through Whatman paper.

Pre-test Processing

Porous discs, 1.5-in. OD and 15 bar, were pre-saturated with the simulated brine. The discs were calibrated for resistance so that 2-terminal resistivity results could be computed for back-up purposes. However corrections for disc resistance are not required for the 4-terminal measurements. To achieve the necessary corrections, stable porous disc resistances are recorded when both the upstream and downstream end-stems are brine-filled. The resistances are also measured when the upstream and downstream

sections are filled with oil and brine, respectively. With the aid of a syringe and needle, upstream dead volume is recorded for subsequent volume corrections and to judge the effectiveness of removal of wetting phase from the upstream end-stem prior to the start of drainage.

Frozen samples were mounted in hydrostatic cells at 400 psig and allowed to thaw. Miscible flow-through cleaning was accomplished by alternately flowing toluene and methanol until produced solvent indicated no traces of crude oil or salt remained in the pore system. Toluene removed crude oil from the core while methanol leached the core of salts. During the flow process, back pressure of up to 200 psig was applied to ensure solvent application to all internal surfaces. Flow rates were maintained between 1-3 cm^3/min. and flow stopped periodically for all diffusion processes to be effective. The period is called "soak period". The flow-cleaned, brine saturated samples were placed in a humidity-controlled oven to constant weight using 40% relative humidity and temperature of 140°F.

Permeability to air at 400 psig and the designated hydrostatic confining stress were determined using ultra permeameter. During the same loadings, pore volumes were determined using helium and Boyle's law porosimeter. Immediately after these tests, sample dimensions were calipered to provide preliminary bulk volume, V_b values for initial permeability and porosity calculations. Later, the samples were frozen, the mounting materials removed and dimensions re-measured. An average of 4-6 measurements of each dimension was considered. The pretest permeability porosity values were recomputed based on the new dimensions. The samples were submerged in a container of synthetic test brine and exposed to vacuum for 3-5 min. so as to partially saturate the pore space in preparation for quick-freezing and subsequent construction of the text assemblies. The assemblies were loaded into the appropriate hydrostatic core cells.

Prior to measurements, an initial hydrostatic pressure of 400 psig was applied using refined oil as the hydraulic medium and the sample allowed a minimum of one hour to thaw. Additional confining stress of 400 psig was incrementally applied every 20 min until the specified confining stress was attained.
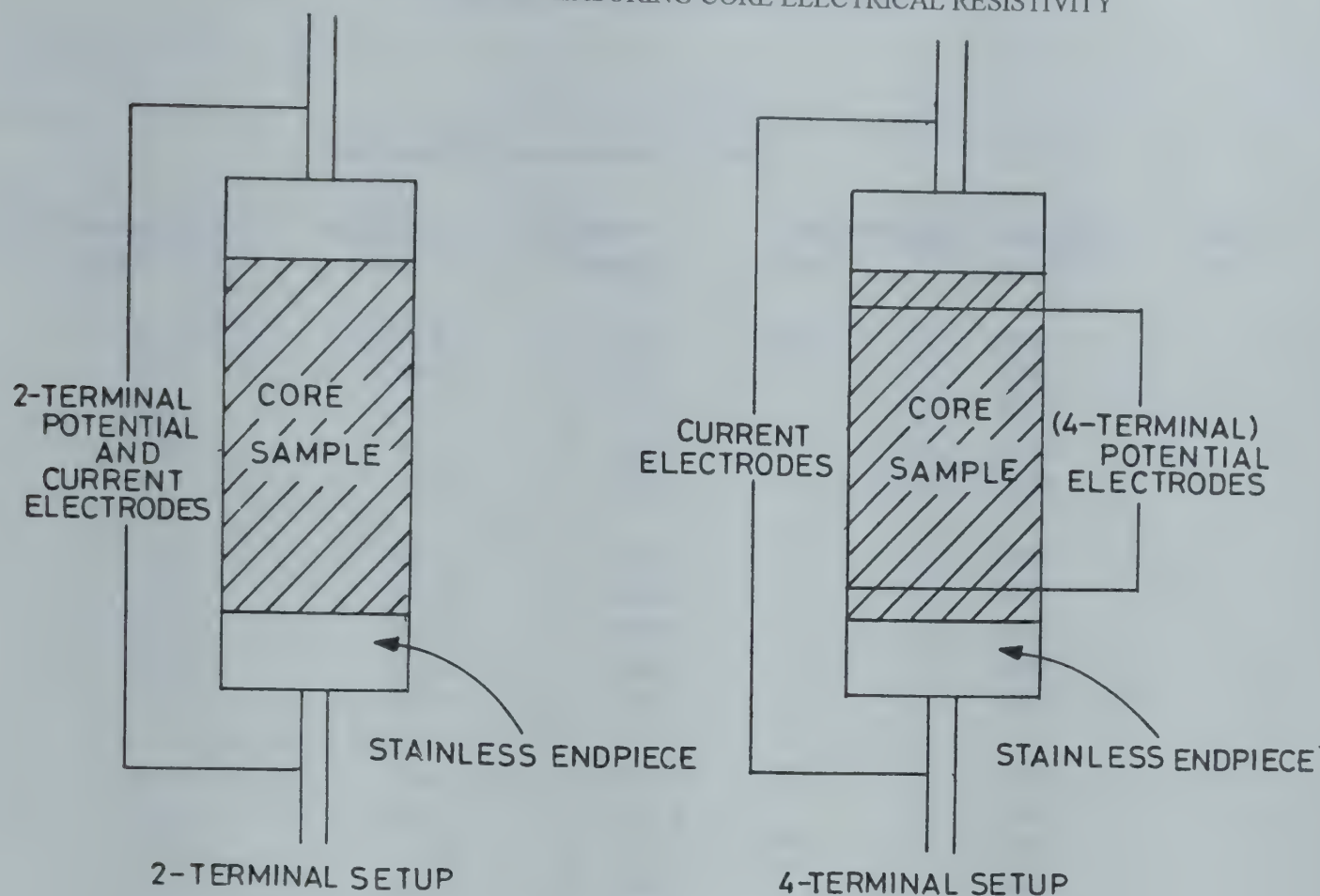
Fig. 1–Schematic diagrams of 2- and 4-terminal systems

Measurement Procedures

To measure rock resistivity, a plug sample was placed between two electrodes and a current passed from one end to the other. The voltage drop between the two electrodes was determined and that value along with the voltage of a parallel resistor used to determine the resistance, from Ohm's law ($V = IR$). Brine is a good conductor, so it was flown at low constant rate through each sample assembly at 200 psig back pressure. The flow was continued until the pore system was gas-free as indicated by constant volume in a gas trap downstream of the back pressure device. At gas-free condition, 2-4 pore volumes of brine were flown each day until daily resistance values stabilized. The stabilized resistivity value prior to drainage was the rock resistivity, R_o. The sample resistance increased as drainage increased due to the displacement of brine by oil in the pore spaces. The frequency used for the text was 10 KHz, since at that frequency the phase shift is minimal.

Figure 1 shows the schematic diagrams of both the 2-electrode and 4-electrode system. In the 2-electrode system, the power producing (current) and voltage measurement (potential) electrodes are both at the ends of the sample. Resistance was then measured from one end of the sample to the other. A 4-electrode system has the voltage measurement electrodes separate from the current electrodes. The current electrodes are at the ends of the sample, but the voltage measurement electrodes are at a given distance from the ends of the sample. In addition to greater accuracy, the 4-electrode system is more appropriate for all unconsolidated cores, since it reduces the problem of end-face of electrode conduction. The surfaces of the sand grains of unconsolidated samples are very rough and without proper instrumentation, the end-face problems are multiplied.

Post-test Processing

At the conclusion of drainage, the upstream and down-stream valves were closed and plumbing disconnected. The upstream valve was then opened to allow the pore pressure to deplete. The confining pressure was then released and the sample assembly removed from the core cell. Samples were then inserted in pre-weighted glass extraction thimbles and a Dean-Stark distillation-extraction performed using pre-distilled toluene. Low volume water traps were used to

Table 1—Formation resistivity factor results

Sample no.	Pressure (psig)	Air permeability (mD)	Porosity (fraction)	Formation factor, f	Cementation factor, m
1	400	2930	0.371	4.59	-1.54
	1000		0.360	4.94	-1.56
	1500		0.352	5.08	-1.56
	2000		0.346	5.31	-1.57
	2500		0.342	5.45	-1.58
2	400	83	0.253	10.80	-1.73
	1000		0.246	11.32	-1.73
	1500		0.243	11.67	-1.74
	2000		0.240	12.03	-1.74
	2500		0.238	12.17	-1.74
3	400	3410	0.350	5.07	-1.55
	1000		0.333	5.90	-1.61
	1500		0.315	6.43	-1.61
	2000		0.305	6.90	-1.63
	2500		0.296	7.25	-1.63
4	400	2430	0.350	5.68	-1.65
	1000		0.333	6.30	-1.67
	1500		0.325	6.68	-1.69
	2000		0.320	6.85	-1.69
	2500		0.318	6.97	-1.69
5	400	824	0.314	6.71	-1.64
	1000		0.302	7.13	-1.64
	1500		0.296	7.34	-1.64
	2000		0.291	7.53	-1.64
	2500		0.287	7.74	-1.64
6	400	764	0.306	6.84	-1.62
	1000		0.303	7.14	-1.65
	1500		0.292	7.64	-1.65
	2000		0.288	7.82	-1.65
	2500		0.284	8.18	-1.67
7	400	4900	0.349	4.73	-1.48
	1000		0.332	5.10	-1.48
	1500		0.322	5.46	-1.50
	2000		0.316	5.62	-1.50
	2500		0.310	5.88	-1.51
8	400	249	0.285	8.67	-1.72
	1000		0.274	9.36	-1.73
	1500		0.273	9.44	-1.73
	2000		0.268	9.81	-1.73
	2500		0.264	10.17	-1.74

Table 2—Resitivity index results

Sample No	Air permeability (mD)	Porosity (fraction)	Pressure (psig)	Saturation	Resistivity index	Saturation exponent, n
1	2930	0.371	1	0.98	1.04	-1.94
			3	0.73	1.87	-1.99
			6	0.27	11.98	-1.90
			16	0.15	53.95	-2.10
			30	0.12	99.92	-2.17
			50	0.10	132.89	-2.12
2	83	0.253	1	0.98	1.04	-1.94
			3	0.95	1.10	-1.86
			6	0.68	2.01	-1.81
			16	0.53	2.91	-1.68
			30	0.45	4.15	-1.78
			50	0.42	4.57	-1.75
3	3410	0.35	1	0.97	1.06	-1.91
			3	0.91	1.21	-2.02
			6	0.52	4.05	-2.20
			16	0.26	15.34	-2.03
			30	0.15	46.85	-2.03
			50	0.10	83.94	-1.92
4	2430	0.35	1	0.97	1.06	-1.91
			3	0.85	1.43	-2.20
			6	0.25	15.93	-2.00
			16	0.14	89.22	-2.28
			30	0.11	157.62	-2.29
			50	0.10	172.24	-2.24
5.	824	0.314	1	0.98	1.04	-1.94
			3	0.92	1.19	-2.09
			6	0.56	2.92	
			16	0.32	7.62	-1.78
			30	0.24	15.89	-1.94
			50	0.19	28.06	-2.01
6.	764	0.306	1	0.98	1.04	-1.94
			3	0.89	1.24	-1.85
			6	0.40	5.10	-1.78
			16	0.25	11.92	-1.79
			30	0.18	21.25	-1.78
			50	0.15	31.74	-1.82
7.	4900	0.349	1	0.97	1.06	-1.91
			3	0.86	1.35	-1.99
			4	0.33	8.75	-1.96
			16	0.15	21.71	-1.84
			30	0.09	99.96	-1.91
			55	0.07	153.17	-1.89
8.	249	0.285	1	0.98	1.04	-1.94
			3	0.90	1.20	-1.73
			6	0.54	3.04	-1.80
			16	0.42	4.75	-1.80
			30	0.36	6.07	-1.77
				0.33	7.55	-1.82

Table 3–Initial water saturation values for both Dean and drainage methods

Sample no.	1	2	3	4	5	6	7	8
Drai-nage	0.10	0.42	0.10	0.10	0.19	0.15	0.07	0.33
S_{wi} Dean Stark	0.10	0.43	0.10	0.11	0.18	0.16	0.08	0.31

Table 4–Resistivity index values from 2- and 4-electrode systems

Sample no.	Saturation, Fraction	Resistivity	Index
		2T	4T
1	0.98	1.05	1.04
	0.73	1.87	1.87
	0.27	12.01	11.98
	0.15	55.36	53.95
	0.12	100.20	100.92
	0.10	141.22	132.89
2	0.98	1.04	1.04
	0.95	1.20	1.10
	0.68	2.06	2.01
	0.53	3.01	2.91
	0.45	4.16	4.15
	0.42	4.63	4.57

improve accuracy of reading small volumes of produced water. After water extraction, the toluene was replaced with methanol and the same distillation equipment used to remove residual salt. The samples were dried to stable weights in a convection oven at 105°C.

The pre-test techniques, equipment and confining pressures were used to determine permeability to air and direct pore volume by Boyle's law. Mounting materials were then carefully removed, all grains collected and grain volume determined in a matrix cup using a Boyle's law device. Bulk volume for each sample was obtained by summing the pore and grain volumes.

Analysis of Results

Formation resistivity factor results are presented in Table 1 and Table 2. Resistivity index results are
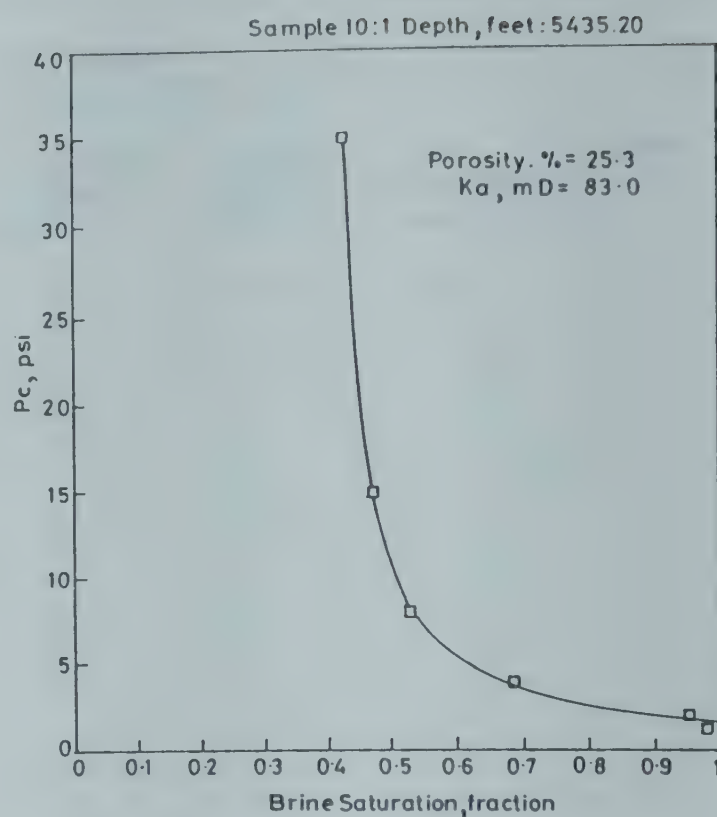
Fig.2–Porous plate capillary pressure at overburden conditions

shown for 8 samples each. Table 3 and 4 give the drainage/Dean-Stark comparisons of water saturation for the 8 core samples and two-and four-electrode resistivity measurements for the first two samples (1 and 2), respectively. Figure 2 is a plot of capillary pressure diagram at overburden conditions for 25.3% porosity and air-permeability of 83. 0 mD

Initial water saturation, S_{wi} values at 50 psig equilibrium point showed very close similarities. The maximum difference is 0.2 units (2%) for sample No. 8 (Table 3). Pore volumes (PVs), water saturation values, capillary pressure and resistivity values at equilibrium state for each pressure point were calculated. Sharp changes in PVs and resistivity were sometimes noted between atmospheric and 400-psig confining pressure. Such changes could be a result of poor electrode contact, the presence of a brine layer in the periphery of the core, or disorientation of the core matrix caused by the low confining pressure. To avoid these problems, the baseline for comparisons was selected to be 400-psig at room temperature.

Measurements at higher pressures (2500 psi, 74°F) indicated that both m and n were considerably higher

than at the baseline condition (400 psi, 74°F). On the other hand, m was lower and n higher at a higher temperature (400 psi, 150°F) than at the base conditon. The results presented in Table 1 and 2 are for the four-electrode system. Improving the technique and quality control reduces disparities in laboratory measured brine resistivity, core saturation and cementation exponent. This is achieved by proper method of preparing brine and instrumentation during actual measurements.

The two-and four-electrode methods of resistivity measurements on samples 1 and 2 were compared and shown in Table 4. When 4T was plotted against 2T, these data were clearly skewed. Many points were very close to the equivalue line, with most of them below it. This implies that the two-electrode method sometimes yields higher resistivity values. The capillary pressure curve for sample 2 shown in Fig. 2 gives a good trend applicable to homogeneous samples.

Anomalous behaviour was observed from the interference between electrodes, when located too close together, and from electrode contact problems. The 4-electrode system ensures friable sample integrity throughout the measurement period. The loading of unconsolidated samples during measurement is improved and the sample is not damaged.

Conclusions

Based on the laboratory measurements of electrical resistivity under confining pressures from 400 to 2500 psig and temperatures from 68 to 80°F, the following conclusions can be drawn:

1. Special core analysis has been improved on the Niger Delta Samples by the use of 4-electrode system instead of the already existing 2-electrode system.

2. Frequency does not affect the 4-electrode measurements. In the 2-electrode method, higher frequencies (between 0.12 and 10 KHz) yield higher resistivity indices when the distance between electrodes is small.

3. There is only a small increase in cementation factor and no remarkable trend of saturation exponent, with increase in confining pressure.

4. Change in temperature only slightly affects cementation factor, m, while resistilvity index and saturation exponent decrease at increasing temperature. The decrease is however gradually smaller at higher temperatures.

Nomenclature

F	formation resistivity factor
I	resistivity index
K	permeability, mD
m	cementatioin factor (exponent)
n	saturation exponent (index)
$R_o, R_w,$	resistivity of 100% brine-saturated sample,
R_t	water and total resistivity, respectively, Ohm-m.
w	water (brine) saturation, percent
ϕ	porosity, percent

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Apple Jelly : Preparation from Different Sources

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A desirable characteristic of the extract for the preparation of apple jelly could be obtained by boiling fruit slices and pomace with water in the ratio of 1:1 for 25 and 35 minutes, respectively. All jellies prepared irrespective of raw materials obtained sensory mean score of more than 5(like slightly) for colour, flavour, taste, texture and overall acceptability; therefore, each treatment could be used for the preparation of jelly. The jelly prepared from fruit extract was most expensive as compared to concentrate and pomace based jellies.

Apple (*Malus domestica* Borkh) is a principal horticultural crop of temperate region of the world. In India, it is being cultivated in Himachal Pradesh, Jammu and Kashmir and hills of Uttar Pradesh. Apple production is primarily aimed at (a) table purpose and (b) processing. The objective of processing of apple is to produce juice in single strength or concentrated form. An insignificant proportion is also utilized for the production of preserves like jam, jelly, fruit leather and candy. However, Eipeson and Bhowmik (1992) listed output and share of jams, jellies and marmalades under FPO licences in 1986 as 18,857 metric tonnes comprising of 12.55 per cent[1].

Among preserves, fruit jelly possesses delicacy and is considered to be a fancy item. However, it is rarely produced in any of the fruit processing factories due to lack of technical knowhow about exact/proper gel forming conditions. Fresh apple and apple pomace (waste) are good sources of pectin[2], which has important nutritional and technological properties[3], being rarely utilized. There is an urgent need to develop a product like jelly to utilize surplus apple and pomace during peak season and regulate

its availability during scarcity. The present investigation was therefore, undertaken to standardize techniques for the preparation of jelly from fresh apple, pomace and concentrate.

Materials and Methods

Materials — Golden Delicious apples were purchased from the local retail market. Apple pomace and juice concentrate (brand name 7-in-1) were procured from Himachal Pradesh Horticultural Produce Processing and Marketing Corporation, Parwanoo.

Preparation of Jelly Extracts — Fruits were washed, cut into slices and kept in air for 20 minutes for enzymatic browning. Jelly extracts were prepared from these slices and pomace as well; by adding water according to treatment (Table 1), boiling in stainless steel pan over a single cylinder LPG burner and filtering through muslin cloth. Apple juice concentrate was diluted by factor method (Table 1). The extracts obtained were evaluated for soluble solids content (SSC). The jelly factor was also calculated (Barwal, 1995) for each treatment[4].

Preparation of Standard Jellies — Sugar was added to the extract from each treatment according to jelly factor (Table 2) and cooked in a stainless steel pan over a single cylinder LPG burner. During cooking, when jelly was semi-viscous, a calculated quan-

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Table 1 — Components for preparation of extracts in various treatments

Treatment	Ingredients		Boiled for (minutes)
	Raw material (gm)	Water (ml)	
T₁	Apple = 1000	2000	25
T₂	Apple = 1000	1500	25
T₃	Apple = 1000	1000	25
T₄	Apple = 1000	750	25
T₅	Pomace = 1000	2500	35
T₆	Pomace = 1000	2000	35
T₇	Pomace = 1000	1500	35
T₈	Pomace = 1000	1000	35
T₉	Concentrate = 100	196	-
T₁₀	Concentrate = 100	270	-
T₁₁	Concentrate = 100	394	-
T₁₂	Concentrate = 100	640	-

Table 2. Formulation and ingredients used for preparation of (one kg) apple jelly from different extracts

Treatment	Extract characteristic		Ingredient added		
	Extract used (gm)	Jelly factor	Sugar (gm)	Citric acid (gm)	Pectin (gm)
T₁	1201.5	204.9	586.3	5.0	3.5
T₂	922.9	157.4	586.3	5.3	3.4
T₃	827.0	141.0	586.3	5.3	3.3
T₄	767.2	130.8	586.3	5.1	3.2
T₅	2358.5	402.3	586.3	2.4	2.4
T₆	2015.2	343.7	586.3	2.8	2.2
T₇	1707.2	291.2	586.3	2.0	2.1
T₈	1415.1	241.4	586.3	3.0	2.1
T₉	254.7	43.4	586.3	6.0	6.7
T₁₀	318.4	54.3	586.3	6.0	6.7
T₁₁	424.5	72.4	586.3	6.0	6.7
T₁₂	636.8	108.6	586.3	6.0	6.7

tity (after subtracting contents in the extracts) of citric acid and pectin (150 grade) were added so that standard/uniform product could be prepared from all sources. Cooking was stopped at 65 ± 1° Brix.

Physico-chemical Determinations — Specific gravity was determined by water displacement method for fruit and by specific gravity bottle method in case of pomace and concentrate. SSC was measured in an Abbe type refractometer and expressed as °Brix. Titrable acidity (TA) was determined by volumetric method and expressed as per cent malic acid (% MA). The pH was recorded with the help of Systronics pH meter. Reducing and total sugars were determined according to the method suggested by Lane and Eynon (1923) and expressed in percentage[5]. Total solids were determined by drying in an oven and expressed in percentage[6]. Minerals were estimated after digestion of samples by wet method (Ranganna, 1986) and calculated in accordance with instrument's standardization. Calcium was determined using Flame Photometer, Eppendorf Geratebau, Germany. Magnesium and iron were estimated in Atomic Absorption Spectrophotometer, AA-175 series (varian), Australia. Sodium and potassium were estimated in Flame Photometer, Evans Electroselenium Ltd, England.

Sensory Evaluation — Jelly samples were presented for sensory evaluation viz. colour/appearance, flavour/aroma, taste, texture and overall acceptability on 9-point (1 = dislike extremely; 9 = like extremely), Hedonic scale[7] by a panel of 25 judges. The judges were selected at random and were same for all the evaluations.

Economics — The economics was worked out based on the cost of all the ingredients plus 20 per cent cost of processing. To reduce error, the per unit cost was determined on the bulk (10 kg) basis.

Statistical Analysis — The data were analysed according to the randomized block design and procedure of Panse and Sukhatme (1967)[8].

Results and Discussion

Proximate composition values of juice concentrate were higher (Table 3) as compared to pomace and fruit. The concentrate had been prepared by evaporating moisture to a level where its contents get concentrated thereby, increasing its share as compared to juice[9]. Mineral content of pomace was

Table 3 — Proximate composition of apple fruit, pomace and concentrate per 100 gm

Characteristics	Fruit	Pomace	Concentrate
Specific gravity (wt/vol)	0.79±0.03	1.03±0.04	1.44±0.02
SSC (°Brix)	12.50±1.25	9.80±0.75	74.00±0.20
Total solids (%)	15.50±1.15	28.90±2.87	76.00±0.40
Total sugars (%)	9.59±0.71	8.34±0.93	57.50±1.30
Reducing sugars (%)	7.46±0.14	6.21±0.41	41.12±0.95
pH	3.28±0.35	2.80±0.25	3.65±1.00
Acidity (% MA)	0.28±0.05	0.57±0.13	1.42±0.08
Calcium (mg)	3.15±1.50	10.93±3.72	22.10±2.43
Magnesium (mg)	4.12±0.85	3.64±0.91	18.37±1.49
Iron (mg)	0.32±0.07	0.41±0.10	1.84±0.70
Sodium (mg)	2.07±0.05	16.44±0.74	11.02±0.05
Potassium (mg)	104.50±3.47	173.00±13.90	684.00±7.50

Table 4 — Physico-chemical characteristics of jelly extracts prepared from different sources

Source	Treatment	Extract yield (gm)	SSC (°Brix)	TA (%MA)	pH
Apple fruit	T_1	1325.0	5.33	0.183	3.83
	T_2	1008.33	6.90	0.203	3.15
	T_3	811.67	7.70	0.223	3.08
	T_4	616.67	8.30	0.270	3.00
	CD at 1%	52.18	0.35	0.020	0.21
Apple pomace	T_5	1040.00	2.70	0.203	2.97
	T_6	783.33	3.20	0.220	2.77
	T_7	583.33	3.70	0.247	2.70
	T_8	466.67	4.50	0.297	2.47
	CD at 1%	64.45	0.26	0.021	0.17
Apple concen.	T_9	296.00	25.00	0.479	2.85
	T_{10}	370.00	20.00	0.384	3.00
	T_{11}	494.00	15.00	0.288	3.15
	T_{12}	740.00	10.00	0.192	3.35

higher than that of fruit. Pomace, the leftover material after extraction of juice, mainly contained peel which is a rich source of minerals[10,11].

Chemical Characteristics of Jelly Extracts — As the amount of water added to a fixed quantity of fruit and pomace decreased (Table 1), yield of extract also decreased significantly (Table 4). With the decrease in extract yield, the SSC increased significantly both in fruit as well as pomace extracts (Table 4). An insignificant increase was also noticed in TA between the extracts i.e. T_1 & T_2, T_2 & T_3, and T_5 & T_6. Concentrate diluted with factor method yielded extract in ascending order and SSC and TA contents in descending order (Table 4).

Jellies prepared from these extracts (Table 2) were compared for

i) **Sensory Characteristics** — T_3 obtained highest score for colour, flavour and taste (Table 5), however, the difference was non-significant as compared to T_1, T_2 and T_4; and significant from rest of treatments. T_{12}, T_{11}, T_{10} and T_9 obtained intermediate values for colour and flavour and were statistically at par. It showed that jelly prepared from fruit extract had good colour, flavour and taste acceptability fol-

lowed by concentrate and pomace. It might be due to the fact that uncontrolled and undesirable reactions took place in pomace, which lowered acceptability[10] whereas, in concentrate, amino-acids, reducing sugars and organic acids polymerize, producing pigments[9] and lost volatile flavouring compounds during evaporation process[12].

Highest texture score was obtained for T_7 and lowest for T_9 (Table 5). T_1, T_2, T_3, T_4, T_7 and T_8 were statistically at par and differed significantly from rest of the treatments. The texture of pomace and fruit jellies was significantly better as compared to concentrate jelly. Pectin is a naturally occurring polysaccharide found in apple peel and subsequently in pomace which improve the setting of the jelly (Jain *et al.* 1984). Panelists showed highest overall acceptability for T_3 followed by T_4 and T_2. Apple fruit jellies (T_1, T_2, T_3 & T_4) were statistically non-significant but differed significantly from pomace and concentrate jellies.

ii) **Mineral Composition** — Calcium and sodium contents were significantly higher in pomace jellies as compared to fruit jellies (Table 6), while, concen-

Table 5 — Mean score of sensory characteristics for jellies from different sources

Treat-ment	Characteristics				
	Colour/ appearance	Flavour/ aroma	Taste	Texture	Overall acceptability
T₁	8.20	7.80	7.60	7.40	7.75
T₂	8.40	8.20	7.80	7.60	8.00
T₃	8.80	8.60	8.40	8.00	8.45
T₄	8.60	8.40	8.20	7.80	8.25
T₅	6.20	4.20	5.20	6.20	5.45
T₆	6.40	4.40	5.60	6.40	5.70
T₇	6.60	4.60	6.00	8.60	6.45
T₈	6.80	4.80	6.40	8.40	6.60
T₉	6.80	5.80	5.20	3.60	5.30
T₁₀	7.00	6.20	5.60	4.20	5.75
T₁₁	7.20	6.60	5.80	5.20	6.20
T₁₂	7.60	6.20	5.40	5.60	6.15
CD at 1%	1.06	1.23	1.35	1.20	1.79

Table 6 — 1 Mineral composition of jellies prepared from different sources (mg/100 gm)

Treat-ment		Calcium (gm)	Mag-nesium (gm)	Iron (gm)	Sodium (gm)	Potas-sium (gm)
Apple	T₁	2.91	3.09	0.21	1.80	79.50
	T₂	2.82	3.00	0.18	1.74	70.70
	T₃	2.77	3.19	0.17	1.70	65.00
	T₄	2.63	3.27	0.17	1.70	65.50
Pomace	T₅	28.10	6.18	0.65	26.09	296.50
	T₆	26.58	6.53	0.63	25.89	267.00
	T₇	24.15	6.82	0.60	25.84	255.00
	T₈	22.23	7.03	0.57	25.80	252.00
Conc.	T₉	18.87	15.76	1.59	9.04	586.00
	T₁₀	18.79	15.64	1.57	8.83	587.00
	T₁₁	18.74	15.61	1.57	8.80	585.00
	T₁₂	18.74	15.50	1.57	8.80	585.00

Conc. = Concentrate

Table 7 — Economics of jellies prepared from different sources

Ingredient	Rate	Apple fruit jelly (10 kg)		Pomace jelly (10 kg)		Concentrate jelly (10 kg)	
		Quantity required	Amount Rs	Quantity required	Amount Rs	Quantity required	Amount Rs
Apple fruit	12/kg	10.20 kg	122.40	-	-	-	-
Pomace	0.5/kg	-	-	30.30 kg	15.15	-	-
Concentrate	103/kg	-	-	-	-	0.86 kg	88.58
Sugar (trust)	16/kg	5.86 kg	93.84	5.86 kg	93.84	5.86 kg	93.84
Pectin (150 grade)	0.38/gm	35.00 gm	13.30	22.00 gm	8.36	67.00 gm	25.46
Citric acid	0.29/gm	53.40 gm	15.49	29.60 gm	8.58	59.80 gm	17.34
Sod. benzoate	0.28/gm	2.00 gm	0.56	2.00 gm	0.56	2.00 gm	0.56
Glass jar	4.60/jar	20 Number	92.00	20 Number	92.00	20 Number	92.00
Total cost of ingredients			337.59		218.49		317.78
Processing cost @ 20%			67.52		43.70		63.56
Total prepara-tion cost			405.11		262.19		381.34
Total yield (10 kg)			20 Jars		20 Jars		20 Jars
Cost/jar or 500 gm pack			20.26		13.11		19.07

trate jellies had intermediate values. High calcium and sodium contents in pomace jellies might be due to the presence of calcium pectate and sodium ions in the peel of the fruit (Bramlage *et al.* 1990)[13]. Magnesium, iron and potassium contents were highest in concentrate jellies followed by pomace and fruit jellies (Table 6). The possible reasons might be that magnesium, iron and potassium get extracted in the juice and concentrated during evaporation.

iii) Economics —Fruit jelly was most expensive costing about Rs 20.26 per 500 gm jar as compared to concentrate and pomace based jellies (Table 7). The overhead expenses viz. labour, interest on capital, depreciation on equipments and/or building etc. have not been taken into consideration. The per unit cost worked out and reported herein for different types of jellies are for the purpose of comparison only.

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Effect of Oxidized Starch and Urea-formaldehyde As Wet-end Additives in Egyptian Bagasse Based Paper

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Oxidized starch was used as strength promoter for paper sheets prepared from unbleached bagasse pulp. The best results were obtained by adding 2% oxidized starch [with 8g active (Cl/l]. At this optimum addition, breakinglength increased to 55% and burst factor increased to 49%. Comparison between native and oxidized starch has been investigated and discussed. Addition of urea- formaldehyde during paper-making considerably improved the retention of filler by unbleached bagasse pulp. Besides promoting filler retention, urea-formaldehyde improved strength and optical properties of the paper produced.

Introduction

In Egypt, agricultural residues are the main lignocellulosic source for paper manufacturing. Egyptian bagasse represents one of the most important sources presently being used for pulp and paper industry. As the quality of the paper produced from bagasse pulp is inferior to that obtained from wood pulp, numerous methods[1,2] have been used to improve paper properties. Starch and modified starch have been used as strength improvement additives[3]. Urea-formaldehyde resin is a synthetic resin which is used for improving wet-strength of paper, namely the tensile and bursting strength of paper[4]. The present research has studied the influence of such additives on the properties of the paper made from Egyptian unbleached kraft bagasse pulp.

Experimental

Raw Material

The raw material selected for paper-making was the unbleached kraft bagasse pulp provided by "Edfo Pulp Co., Upper Egypt".

Preparation of Oxidized Starch

Maize starch oxidized with 4,6 and 8g active Cl/l using sodium hypochlorite solution at pH 7 and liquor ratio 1:10 (ref. 5) for 2h at 25°C under stirring.

then filtered, washed thoroughly with distilled water and dried at room temperature.

— Paper sheets were made by the addition of different amounts of oxidized starch (2,4, 6 and 8g/100g pulp) to unbleached bagasse pulp.

— Another set of paper sheets was made by the addition of different amounts of 60% urea-formaldehyde (0.5, 1.00, 1.5 ml) to bagasse pulp in the presence of different amounts of either starch or kaolin (2,4,and 6% based on pulp weight). The produced sheets were heated at 130°C for 3 h.[6]

— The third set of hand sheets was made by the addition of different amounts of starch (2,4, 6 and 8% based on pulp weight) and 15% kaolin to the bagasse pulp.

Preparation of Paper Sheets

In all the experiments, the unbleached bagasse pulp was beaten in a "Vally Beater" till 30°SR. The oxidized starch powder was added to the beaten pulp, then mixed well in a mixer. The pH of the pulp slurry was adjusted to 5-5.5 by the addition of alum. The paper sheets were prepared according to the Swedish Standard Method (SCA), using the model SCA sheet former (ABLorentzen and Wettre). In the apparatus a sheet of 165 mm diam = 214 cm² surface was formed. The weight of oven-dry pulp used for each sheet was 1.43g . After sheet formation, the sheet was

Table 1 — Properties of hand sheets with oxidized starch
           containing rosin size and alum

Amount of oxidized starch added (g/100g pulp)	Breaking-length, m	Tear factor	Burst factor	Bright-ness, %	Printing opacity %
Blank	1892	60	10.81	49	85.91
2	2924	51	16.07	55	96.18
4	2894	49	13.51	56	97.68
8	2811	43	11.94	58	98.27

pressed for 4 min using a hydraulic press. The test pressure was adjusted according to Standard (SCAN: 5kg f/cm^2). The test sheets were dried with the help of rotating cylinder or drum at 60°C + 5°C (SCAN). The drying time was 2h. The sheets were then placed for conditioning, at 65% relative humidity and temperature ranging from 18-20°C.

Testing of Paper

Tensile strength and burst strength were determined according to the German Standard Method[7]. Brightness and opacity were determined by using a " Carl Zeiss El REPHO Tester"

Results and Discussion

1 Properties of Hand Sheets with Oxidized Starch Containing Rosin Size and Alum

Properties of paper sheets prepared from kraft unbleached bagasse pulp containing oxidized starch (oxidized by 8g active Cl/l) are given in Table 1. Addition of oxidized starch improved the breakinglength and the burst factor. The best results were obtained by adding 2% oxidized starch where the breakinglength increased by about 54.5% and the burst factor increased by about 48.6%.

2 Comparison Between Native and Oxidized Starch Regarding Improvement in Strength Properties

Figure (1a) and (1b) show the improvement in breakinglength and burst factor of the paper sheets prepared from unbleached bagasse pulp containing different amounts of oxidized starch (with 4,6, and 8g active Cl/l).

It is evident from Fig. (1a and b) that 2% added oxidized starch represents the optimum addition at
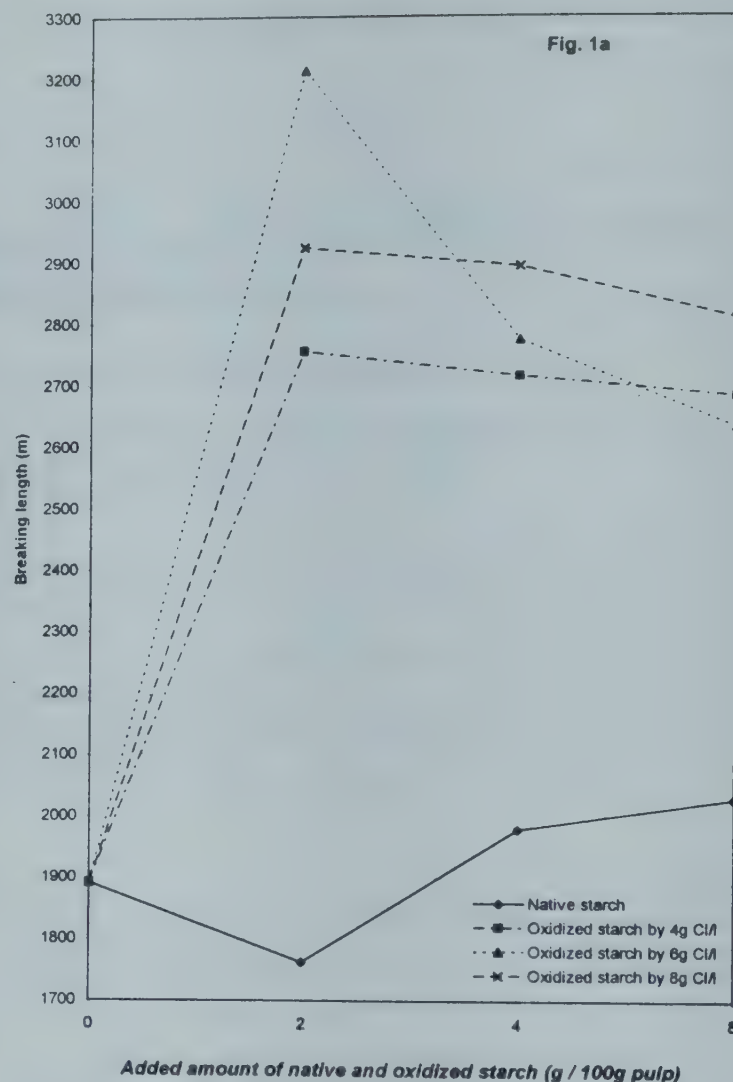
Fig. 1 (a) — Breakinglength of hand sheets with native and oxidized starch

which the best improvement in breakinglength and burst factor was achieved. In the case of oxidation with 4% g/l Cl, the improvement in breakinglength and burst factor was found to be 45.6% and 39%, respectively. In the case of oxidation with 6% g/l Cl, the improvement in breakinglength and burst factor was 70% and 37%, respectively. But in the case of oxidation with 8g/l Cl, the improvement in breakinglength and burst factor was 54.5 and 48.7%, respectively..

From the results , it is evident that oxidation of starch by 6% g/l Cl and by 8% g/l Cl caused much improvement in paper properties, and 2% added amount of oxidized starch gave the best results.

Effect of Addition of Native Starch and (15% Kaolin) on Paper Properties

Starch has been proposed as retention aid for filler[8]. Addition of different amounts of starch (2,4,6, and 8g/100g pulp) with 15% kaolin during paper-
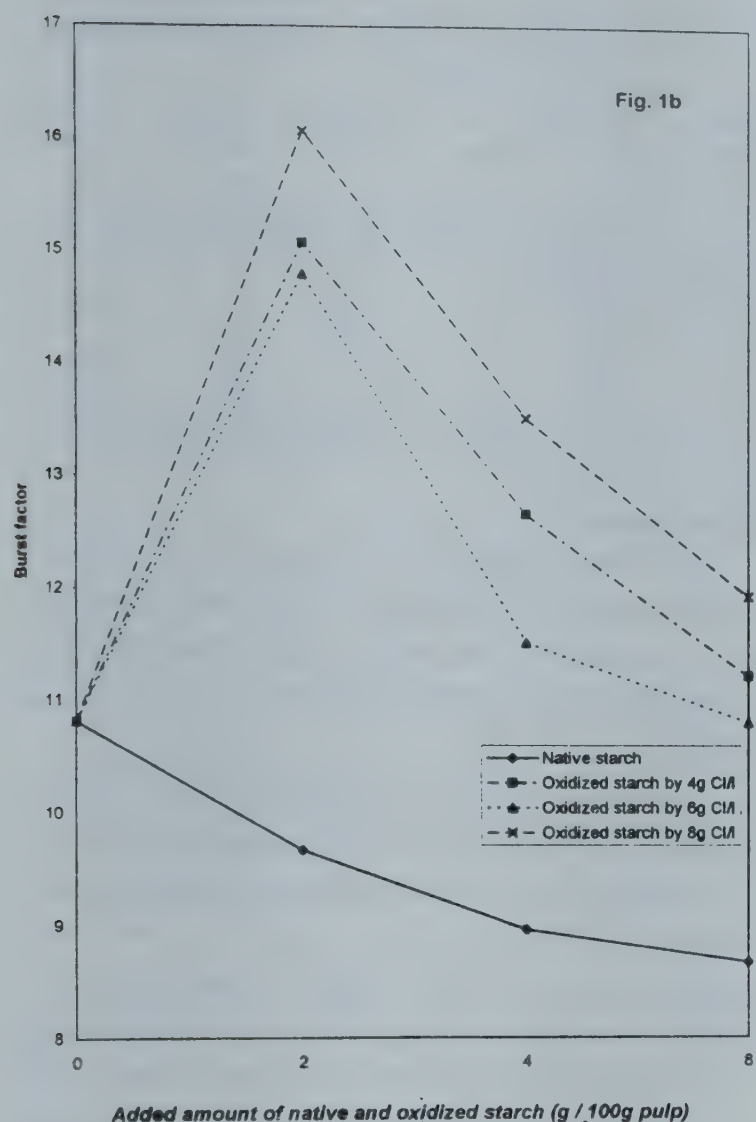
Fig. 1 (b) — Burst factor of hand sheets with native and oxidized starch

Table 2 — Retention of filler with native starch

Added amount of starch (g/100g pulp)	*	**			
	Blank	None	2	4	6	8
Ash content %	2.85	3.93	12.00	11.85	11.00	10.00
Retained kaolin %	—	8.27	70.11	68.96	62.45	54.78

*Without kaolin or starch

**15% kaolin is added without starch

Table 3 — Optical properties of hand sheets with native starch containing 15% kaolin

Added amount of starch (g/100g pulp)	*	**			
	Blank	None	2	4	6	8
Brightness, %	49	53	53	53	53	55
Printing opacity, %	85.91	93.33	94.22	95.11	95.11	96.36

*Without kaolin or starch

**15% kaolin is added without starch

Table 4 — Properties of hand sheets with urea-formaldehyde containing 6% native starch

Urea-formaldehyde (ml)	Breaking-length (m)	Tear factor	Burst factor	Brightness %	Printing opacity, %
Blank	3482	72	21.62	47	85.74
0.5	5302	46	33.28	48	90.74
1.0	5337	49	29.72	49	91.87
1.5	5405	52	28.87	51	91.11

making improved the retention of kaolin by unbleached bagasse pulp as shown from Table 2. It is evident from Table 3 that besides promotion in filler retention, optical properties of the produced paper also improved. The improvement in printing opacity is found to be due to the increase in kaolin retained by unbleached bagasse pulp.

3 Properties of Hand Sheets with Urea-formaldehyde Containing 6% Native Starch

Properties of paper sheets prepared from unbleached bagasse pulp containing different amounts of native starch (2%, 4% and 6% based on pulp) and different amounts of 60% urea-formaldehyde (0.5 to 1.5 ml) were studied. The best results were obtained by adding 6% native starch. At this optimum addition of 0.5 ml urea- formaldehyde breakinglength increased by 52% and burst factor increased by 55%, as shown from Table 4.

The improvement in strength properties which resulted by the addition of urea-formaldehyde resin is due to certain chemical reaction between the urea-formaldehyde resin and cellulose, similar to that obtained between these resins and the other polyhydric alcohols, such as starch and sugar. A considerable improvement in brightness and opacity was also observed.

4 Properties of Hand Sheets with Urea-formaldehyde Containing Different Amounts of Kaolin

A high retention of the filler is essential, so that the loss during paper-making could be reduced as far as possible. The effect of urea-formaldehyde addi-
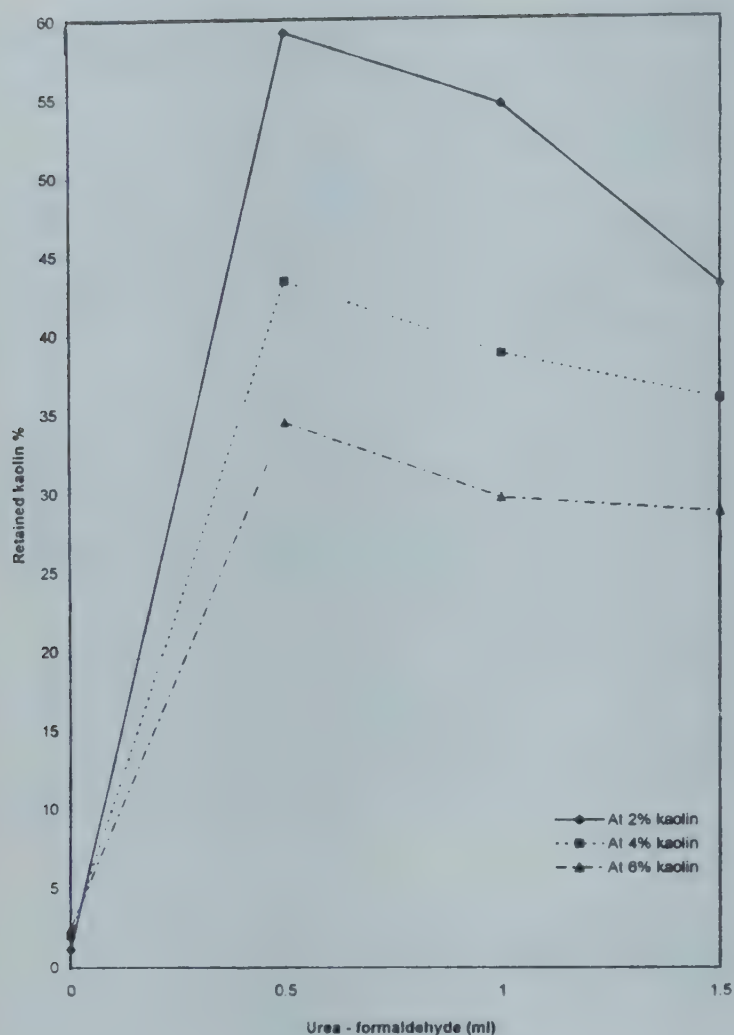
Fig. 2 — Retention of filler with urea-formaldehyde

Table 5 — Properties of hand sheets with urea-formaldehyde containing 4% kaolin

Urea-formalde-hyde (ml)	Breaking-length (m)	Tear factor	Burst factor	Bright-ness %	Printing opacity %
Blank	3482	72	21.62	47	85.74
0.50	4200	60	29.44	53	93.11
1.00	4864	59	28.30	51	92.11
1.50	4921	54	24.75	49	92.33

Conclusions

It is thus concluded that oxidized starch (with 6% and 8% active Cl) resulted in lot of improvement in paper properties than native starch, and the best results were obtained by the addition of 2% oxidized starch.

Addition of native starch promotes filler retention and thus improves the optical properties of the produced paper sheets. Better results in strength properties were obtained when native starch was used in the presence of urea-formaldehyde as compared to the use of urea-formaldehyde with kaolin. Improvement in printing opacity was found to be much more by the use of urea-formaldehyde with kaolin as compared to urea- formaldehyde and starch.

tion on promoting filler retention at different amounts of kaolin (2%, 4%, and 6%, respectively, based on pulp) was studied and is shown in Fig. 2.

The optimum filler retention was obtained by the addition of 2% kaolin and 0.5ml urea-formaldehyde which is evident from Fig.2. The effect of urea-formaldehyde addition on properties of the prepared paper sheets at different amounts of kaolin (2%, 4% and 6%, respectively, based on pulp) was studied. The best results were obtained by the addition of 4% kaolin (Table 5).

It is evident from Table 5 that the addition of urea-formaldehyde and kaolin improved paper strength and optical properties. Addition of 0.5, 1.0, 1.5 ml urea-formaldehyde and 4% kaolin increased the breakinglength by ratio 20.6% , 40%, and 41%, respectively, and the burst factor by ratio 36%, 31%, and 14.5 %, respectively. Also, the printing opacity increased by 9%, 7%, and 7.7 %, respectively.

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Preservation of Talla Bamboo (*Bambusa tulda* Roxb.) by Chromated Copper Arsenate (CCA)

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Researches revealed that the talla bamboo (*Bambusa tulda* Roxb.) in Bangladesh can be full cell pressure treated with CCA in green and dry conditions. The dry bamboo gives higher loading absorptions than green one when impregnated at same treating conditions. Also higher absorptions are obtained at nodes rather than internodes. Adequate penetration and retention results for ground and water contact uses are only possible by treating bamboos predried to 10-15% MC. The green bamboo is easily treatable for indoor and overhead outdoor use. The service life of this socioeconomically important bamboo can easily be increased at least two times than nominal by CCA treating either green or dry bamboo. Two small holes made before pressure treatment in each internode will give split-free bamboo.

According to Prasad[1], talla (*Bambusa tulda* Roxb.), is a native of Assam, Bengal, Northern Cachar, Chittagong and Myanmar. As regards abundance, this species is next to muli (*Melocanna baccifera* (Roxb.) Kurz.) and it is also cultivated in the homesteads of Bangladesh[2]. The bamboo is distributed worldwide, in tropical zone having diversity of uses, important economically and environmentally[3-5]. Rural and urban constructions are mostly dependent on bamboo. The bamboo reserves can be increased 100 per cent if the normal service life is increased two times (e.g. from 2-3 years to 5-6 years in ground contact) by any means as reported by Lahiry[3].

The CCA salt treated bamboo has been used in India as exterior claddings and as roofing support for over 33 years[6]. Such long service life has not been reported when used in ground and water[3]. Like muli (*Melocanna baccifera* (Roxb.) Kurz.) the talla or mitinga falls under thin walled and narrow bamboo group, but stronger than muli due to slightly higher in shell thickness and strong and firm nodes and branches. Both muli and talla act as hollow pipes if nodes are ruptured or perforated from inside. As such both the species have special ground contact use in hilly areas of Bangladesh for using as irrigation pipe.

These bamboo pipes are driven into underground shallow, curved water table and water comes out through bamboo pipes automatically like domestic tap water. Moreover, some narrow bamboos are used in making tents, cottages, water logging fishing masts etc. It is an attempt to find out the distribution of CCA in full cell pressure treated green and air-dried or kiln-dried talla/mitinga bamboo species from Bangladesh for higher service life in ground and water contact uses as well as their treating behaviour. Such work has not been carried out in Bangladesh.

Materials and Methods

Both green and dry round bamboos were full cell pressure treated (length, initial moisture, concentration of CCA-C, amount and duration of vacuum and pressure, bamboo species have been presented in Table 1). The 16% MC in dry bamboo was obtained by kiln-drying the green bamboo with sawn timber at maximum dry bulb temperature of 70°C and wet bulb temperature of 60°C following 7 days schedule only. The pretreatment initial moisture content at middle of bamboo was measured with Delmhorst resistance type moisture meter. The concentration of CCA-C solution was determined by hydrometer as well as by ASOMA X-ray analyzer following stand-

ard method[7]. After preservative treatment, the pene-
tration of copper compound in node and internode of
bottom, middle and top of bamboo was tested from
cross cut samples with the application of standard
reagent Chrom Azurol Solution as per AWPA stand-
ard[8]. The minute penetration (as presented in Table
1, col.e) was determined by hand lens (10x). The dry
oxide retention of CCA-C was determined spectro-
scopically by an ASOMA X-ray analyzer (model
8620) following standard method[7].

In order to control splitting of thin-walled bamboo
(green and dry) during pressure treatment inside the
pressure vessel, two radial holes (6mm dia.) were
made in each internode as earlier reported by Lahiry[3].
One hole was made near the lower node and the other
hole was made near the upper node at 180° apart i.e.
opposite to the first hole of the same internode. Sonti
reported in 1988 that if the septa are drilled through,
round bamboo can be treated quite effectively[9].

Results and Discussion

The results of treatment of both green and dry
bamboo have been presented in Tables 1 & 2 and in
Retention Map and discussed with the revealed treat-
ing behaviours of bamboo as follows under individ-
ual caption:

Revealed Principles in same Treating Conditions

(i) **Dry vs Green Bamboo**: Dry bamboo pene-
trates and retains more than green bamboo (obtained
75 per cent higher penetration and 37.69 per cent
higher retention, Table I & II and Retention map.)

(ii) **Node VS Internode**: Generally the nodal
penetration and retention are more than internodal
(obtained 33.33 per cent higher penetration in dry
bamboo, but exceptionally equal in green bamboo,
and 71.52 per cent higher retention in dry bamboo
and 23.05 per cent higher retention in green bamboo,
Tables - 1 & 2 and retention map).

(iii) **Dry vs Green Node** : Dry nodes penetrate and
retain more than green nodes (obtained 100 per cent
higher penetration and 57.71 per cent higher reten-
tion in dry nodes, Tables 1 & 2 and Retention map).

(iv) **Dry Internode vs Green Internode** : Dry
internodes penetrate and retain more than green in-
ternodes but differences are not as high as nodes
(obtained 50 per cent higher penetration and 13.08
per cent higher retention in dry internodes, Tables 1
& 2 and Retention map).

(v) **Dry Butt vs Green Butt** : Dry butt penetrates
and retains slightly more than green butt (obtained
only 16.66 per cent higher penetration and 5.04 per
cent higher retention, Table 2).

(vi) **Dry Middle vs Green Middle**: Dry middle
penetrates and retains more than green middle (ob-
tained 75 per cent higher penetration and 70.42 per
cent higher retention, Table 2).

(vii) **Dry vs Green Tops** : Dry top penetrates and
retains more than green top (obtained 100 per cent
higher penetration and 47.18 per cent higher reten-
tion, Table 2).

(viii) **Butt vs Middle vs Top:**

A. Dry Bamboo Group: The penetration in butt
and middle were same but higher in top which may
be due to comparatively thin wall at top. Compared
to butt and top, the retention in middle was noted
higher than butt and top (Table 2).

B. Green Bamboo Group : The penetration and
retention in butt was higher than middle and top
(Table 2).

(ix) **Dry vs Green(Chemical Balance)** : CrO_3
retains more in green bamboo than dry bamboo (ob-
tained 47.05 per cent vs 50.61 per cent Table 2).
As_2O_5 retains more in dry bamboo than green bam-
boo (34.28 per cent vs 31.53 per cent, Table 2). CuO
retains more or less equally in both dry and green
bamboo, however green bamboo retains slightly low
and was the lowest in butt (Table 2). In all cases, the
chemical balance of CCA-C was within the range
limit of the type of AWPA standard[10].

For Ground Contact Uses

The highest penetration and retention obtained in
nodes of dry middle and dry top (retention 22.36
kg/m^3 and 20.40 kg/m^3 respectively equivalent to
w/w 4 per cent dry oxides) are the desired adequate
results for ground contact use in Bangladesh, because
similar doses are being used successfully in wooden
utility poles for rural electrification[11]. But similar
doses of penetration and retention are required in
internodes which would be possible by using higher
concentration of CCA-C in dry bamboo only and not
possible in green bamboo. The retention requirement
stipulated in Indian Standard[12] may also be followed.

Table 1 — Treatment Results of CCA-C Treated Bangladeshi Dry and Green, Round, Talla/Mitinga Bamboo (*Bambusa tulda* Roxb.) Full Cell Pressure Impregnated at Same Vacuum, Pressure and Duration.

Treatment Information	Bamboo Length (m)	Pretreatment Moisture Content	Penetration and Retention Results		Retention, day oxide, (kg/m³)				GB to DB Results higher (Retention) (%)
			Test Zones	Penetration	CrO₃	CuO	As₂O₅	Total	
a	b	c	d	e	f	g	h	i	j
Kiln-dried and green bamboo	3.66	DB=16%	DBN	(++++)	7.75	3.29	5.37	16.41	13.33%
treated in same	3.66	GB=38%	GBN	(+++)	7.93·	2.44	4.11	14.48	
treatment charge No	3.66	DB=16%	DMN	(++++)	10.60	4.06	7.70	22.36	90.30%
1160, treated by	3.66	GB=38%	GMN	(++)	5.55	2.31	3.90	11.75	
M/s. Esack Brothers Industries Ltd.	3.66	DB=16%	DTN	(++++)	9.03	3.85	7.52	20.40	80.37%
Chittagong, initial	3.66	GB=38%	GTN	(++)	5.41	2.11	3.79	11.31	
vacuum 600 mm Hg for	3.66	DB=16%	DBIN	(+++)	5.62	2.21	4.06	11.89	– 3.96%
60 min. and impregnation	3.66	GB=38%	GBIN	(+++)	6.37	2.11	3.90	12.38	
pressure of 12.66 kg/cm²	3.66	DB=16%	DMIN	(+++)	6.28	2.23	4.26	12.77	43.97%
for 360 mints, concentration of	3.66	GB=38%	GMIN	(++)	4.54	1.54	2.79	8.87	
CCA-C, oxide of 4.60% (W/V), Rentokil	3.66	DB=16%	DTIN	(++++)	4.85	1.79	3.21	9.85	6.37%
CCA, UK, treated with 1.07 m long anchor logs.	3.66	GB=38%	GTIN	(++)	4.85	1.59	2.82	9.26	

Table 1 — Treatment Results of CCA-C Treated Bangladeshi Dry and Green, Round, Talla/Mitinga Bamboo (*Bambusa tulda* Roxb.) Full Cell Pressure Impregnated at Same Vacuum, Pressure and Duration.   —(Contd)

Calculation and Comparison	MEAN DBN, DMN DTN	(++++)	9.13	3.74	6.86	19.73	Retention 57.71%
	MEAN GBN, GMN, GTN	(++)	6.29	2.29	3.93	12.51	Penetration 100%
	MEAN DBIN, DMIN, DTIN	(+++)	5.58	2.08	3.84	11.50	Retention 13.08%
	MEAN GBIN, GMIN, GTIN	(++)	5.25	1.75	3.17	10.17	Penetration 50.00%
	Dry internode to Node, higher (%)	33.33%	63.51%	80.00%	78.59%	71.52%	–
	Green Internode to Node, higher (%)	000%	19.75%	30.96%	24.15%	23.05%	–
	Green to Dry,,higher (%)	75.00%	27.39%	43.99%	50.85%	37.69%	–

Abbreviations: DB= Dry Bamboo, GB= Green Bamboo, DBN= Dry Butt Node, GBN= Green Butt Node, DNM=Dry Middle Node, GMN= Green Middle Node, DTN= Dry Top Node, GTN= Green Top Node, DBIN= Dry Butt Internode, BGIN= Green Butt Internode, DMIN= Dry Middle Internode, GMIN= Green Middle Internode, DTIN= Dry Top Internode, GTIN= Green Top Internode.

(++++) = Penetration is 100% complete in sampled area.

(+++) = Penetration is 75% complete in sampled area.

(++) = Penetration is 50% complete in sampled area.

Table 2 — Extraction Form Table 1

Test Zones	Penetration	Retention, dry oxide, kg/m^3 (Chemical Balance %)				GB to DB Results Higher (%)
	(%)	CrO$_3$	CuO	As$_2$O$_5$	Total	
a	b	c	d	e	f	g
DBN+DBIN	87.50%	6.69(47.24%)	2.75(19.42%)	4.72(33.34%)	14.16 (100%)	Penetration = 16.66%
GBN+GBIN	75.00%	7.15 (53.04%)	2.28(16.91%)	4.05(30.05%)	13.48 (100%)	Retention = 5.04%
DMN+DMIN	87.50%	8.44 (48.04%)	3.15(17.93%)	5.98(34.03%)	17.57 (100%)	Penetration = 75.00%
GMN+GMIN	50.00%	5.04 (48.88%)	1.93(18.72%)	3.34(32.40%)	10.31 (100%)	Retention = 70.42%)
DTN+DTIN	100.00%	6.94(45.87%)	2.82(18.64%)	5.37(35.49%)	15.13 (100%)	Penetration = 100.00%
GTN+GTIN	50.00%	5.13(49.90%)	1.85(18.00%)	3.30(32.10%)	1.28(100%)	Retention = 47.18%
Chemical Balance, Mean Dry bamboo	47.05%	18.66%	34.28%	99.99%		–
Chemical Balance, Mean Green bamboo	50.61%	17.86%	31.53%	100%		–

Abbreviations: As stated under Table 1.

RETENTION MAP OF DRY & GREEN BAMBOOS

Internode to node, higher (%) →

(38.024%) (75.227%) (107.169%) Mean (71.524%)

(16.418) (11.895) (22.366) (12.764) (20.400) (9.847) =(19.727) (11.501)

Dry →

Mean (31.228)

Green to Dry,higher(%)[Butt] (13.344%)(-3.971%) [Middle](90.381%)(43.998%)[Top] (80.451%)(6.373%) (57.664%)(13.109%)(37.689%)

Green →

Mean (22.680)

(14.485) (12.387) (11.748) (8.864) (11.305)(9.257)= (12.512)(10.168)

Internode to node, higher (%) →

(16.937%) (32.536%) (22.123%) (23.052%) Mean
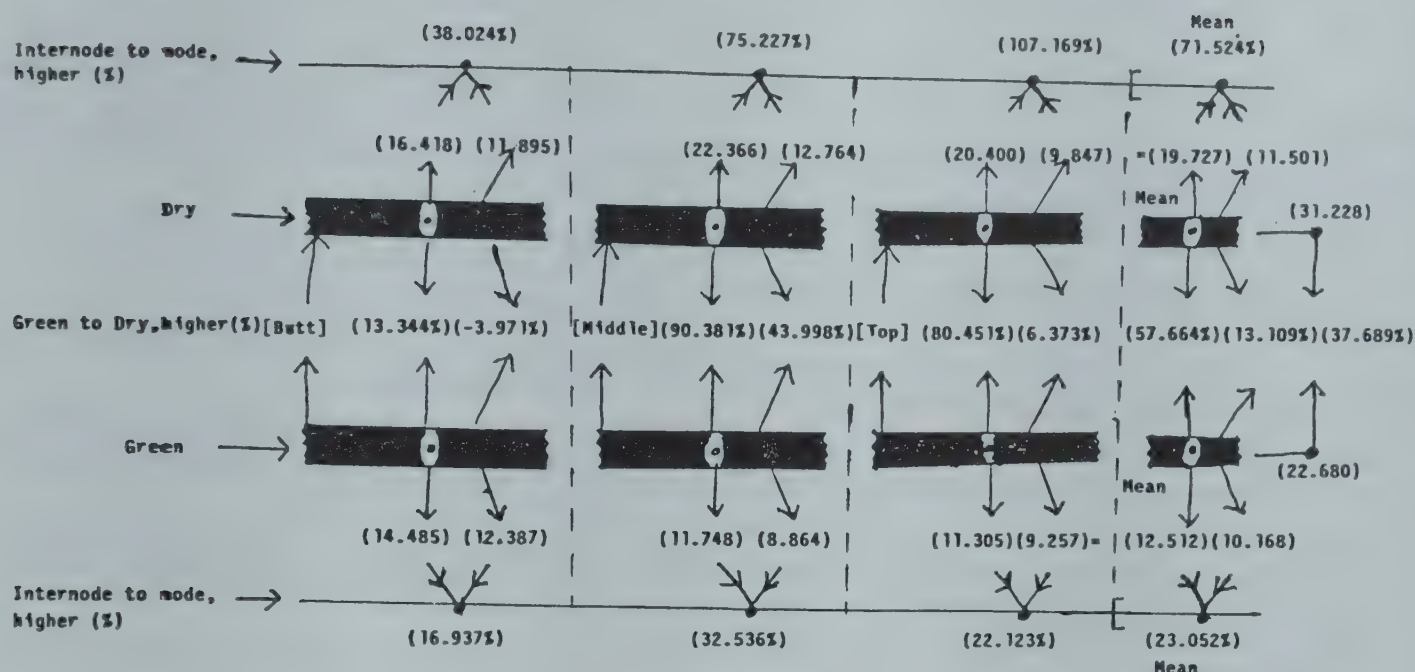
For Indoor and Overhead Outdoor Uses

All penetration and retention results obtained from dry as well as green bamboo are adequate for indoor and overhead outdoor uses, because similar doses are being successfully used for wood products (e.g. crossarms, meter boards etc.) in rural electrification in Bangladesh (in REB)[13,14]. Indian Standard for non-structural bamboo (IS : 1902) may also be followed when applicable[15].

Treatment Group

Treatment group A is defined as the problematic bamboo species where wall/shell thickness being higher (more than 12 mm), can not be treated properly in green condition by full cell pressure method (e.g. all *Bambusa balcooa* and some mature thick walled *B. vulgaris*) and adequate penetration and retention are not possible without kiln-drying[3]. Treatment group B is defined as the nonproblematic bamboo species where wall/shell thickness is comparatively low, can easily be pressure treated in green or dry conditions (e.g. *Melocanna baccifera* and *B. vulgaris*)[3].

Though the wall/shell thickness of *Bambusa tulda* is not as high as those of *B. vulgaris*, the treating behaviours of *B. tulda* resemble with *B. vulgaris*. Therefore, the treatment group for *B. tulda* will be same as *B. vulgaris* and for higher adequate penetration and retention (20 kg/m³ or 4 per cent w/w) for

ground and water contact uses, the bamboo (comparatively thick walled and mature one) must be dried (kiln-drying is preferred) up to 10-15 per cent MC (half of FSP) before full cell pressure treatment with CCA-C, oxides. Revealed that mature round bamboo, predrilled at internodes, can be kiln-dried successfully without collapse. For indoor or overhead outdoor uses, green bamboo can be pressure treated only at 6.4 kg/m³ or 1.25 per cent w/w retention of dry oxides. Treatment of splitted or sliced bamboo would be much more easier and effective.

Conclusion

Thin walled bamboo can be pressure treated even in green condition for lower level of penetration and retention purposes. However, they require to be incised (drilling of holes, see method) to avoid cracking and collapse. Thick walled (more than 12 mm at butt) and mature bamboos require to be dried to about 10-15 per cent MC before subjecting to pressure treatment to get adequate higher retention. Double service life is expected for even bamboo treated at green condition.

Acknowledgement

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for their help during this research works. Thanks to the Editor of the Journal for the kind review of this thesis.

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Weather Resistance of Polyvinyl Chloride — EPDM Rubber Blends

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EPDM rubber was blended with polyvinyl chloride by graft copolymerization, melt mixing and extrusion techniques. Grafting of EPDM rubber with vinyl chloride monomer was carried out by solution polymerization at 70°C in presence of benzoyl peroxide initiator[1]. Grafted rubber was modified with thermal stabilizers and mixed with plasticized PVC in 50:50 and 25:75 phr proportions. Melt mixing followed by extrusion was done for blending the two components. Compression moulded samples of blends were subjected to accelerated weathering in Xenostst 150 S weatherometer under controlled temperature (47 ± 3°C and relative humidity (65%) conditions for 240, 300 and 720 h. Both exposed and unexposed samples were evaluated for their mechanical strength. Blends with higher proportion of ethylene - propylene - ethylidene norbornene rubber (50 phr) had shown better retention upon accelerated weathering tests. Hardness, per cent elongation at break and tensile strength at break of 50:50 phr blend had shown 0.3 per cent, 1 per cent and 8 per cent fall respectively after 720 h of exposure under above conditions. Studies also reveal that notched impact strength of the 50:50 phr proportion of PVC-EPDM containing 50 phr of dioctyl phthalate was not affected at all after 720 h of exposure.

Introduction

EPDM rubber blends with polyvinyl chloride are cost effective as well as possess a set of properties. It not only acts as an impact modifier[2-4] for PVC, but on the other hand imparts weather resistance to it. In addition to this, these blends possess uniformly good processability and heat resistance [5,6]. Weather resistance studies carried out on EPDM-vinyl chloride graft copolymer possessing tensile strength 75 kg/m^2, elongation at break 200% and JIS hardness A 87, after 200 h of irradiation in a weatherometer records 2 per cent, − 8 per cent, and + 2 points of changes[7,8]. Moreover, plasticizer in polyvinyl chloride and softening agents in ethylene propylene diene rubber increases the interfacial thickness and formation velocity between these mutually incompatible, polymers[9]. Graft copolymer of vinyl chloride finds various applications both as laminates and other automobile parts like weather strips[10]. The present studies made in this context deal with the preparation of EDPM-PVC blends by graft copolymerization[1] followed by melt mixing and extrusion. The

weatherometer exposure was carried out for 720 h in mobile condition.

The lower portion of solar spectrum possesses 80-90 K cals/mole of energy and is responsible for the rupture of molecular bonds present in the polymer structure. Although, the ozone level generated by the photolysis of oxygen in the atmosphere is quite low (5-10 ppm) in air[11]. Still, this trace amount is responsible for cracking elastomers and plastics. The cracking phenomenon of elastomers[12] leads to degradation that occurs primarily on the rubber surface and destroys its usefulness. Rubber products are mostly exposed to sun light, as they find many outdoor applications and rubbers like styrene, butadiene etc. contain olefinic chains. The olefinic broken bonds resulting due to ozonolysis cause embrittlement of rubber at latter stage.

There are alternative materials like UV absorbers or antiozonants which are used for protecting the elastomer or plastics that are vulnerable to solar spectrum. There are three classes of antiozonants being used for the purpose: (i) N, N'substituted -P-phenylene diamine (PDA) derivatives that are

$$--(-CH_2-CH_2)_m--(-CH--CH_2)_n--(\underset{q}{})--$$

$$\overset{CH_3}{\underset{|}{}}$$

$$= CH--CH_3$$

(I)
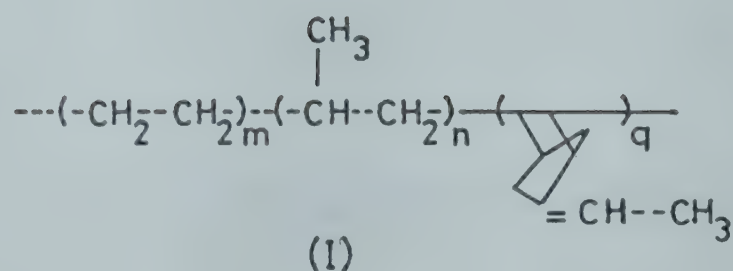
chemically reactive; (ii) microcrystalline or paraffinic waxes, which are unreactive and (iii) ozone resistant elastomers like ethylene propylene diene (EPDM) rubber, polyacrylic rubber, silicone rubber[13] etc. PDA antiozonants when used in suitable quantities diffuse through the surface and preferentially react with ozone, with the result that the rubber is not attacked until the antiozonant is exhausted[14-16]. Waxes on the other hand, bloom through the surface to make a surface film which is thicker than PDAs and thereby ensure better protection[17].

At higher concentrations ozone resistant elastomers serve as the best antiozonants because they blend well with the elastomer or plastic materials forming inter mixed domains inside the molecular arrangement and leads to better retention of mechanical properties under prolonged time span. Ethylene- propylene ethylidene norbornene rubber with a molecular chain having pendant unsaturation leads to better stability of the chain, Vulnerability of the elastomer chain (I) to solar spectrum is therefore not observed. It is reported to possess ozone resistance of high degree.EPDM rubber is blended with polyvinyl chloride having moderately good resistance[18] to yield blends with good flow properties, impact resistance and tensile strength. They were exposed under accelerated artificial weathering conditions in Xenostat weatherometer.

Experimental Procedure

Reaction Materials

EPDM rubber (Royalene, Grade 525) was procured from Uniroyal Chemical Co. Ltd. USA, which had ENB content about 8.5%. Polyvinyl chloride (Grade SR 10 A) and vinyl chloride monomer (VCM) was procured from Shriram Fertilizer and Chemicals, Kota.

Table 1 — Unexposed EPDM rubber-polyvinyl chloride blend samples

EPDM-PVC Graft	PVC*	Chlorine Content of Graft (per cent)	Tensile Strength at Break (kg/cm^2)	Elongation at Break (per cent)	Hardness (Shore A/D)	Impact Strength, Notched kg-cm/cm
50	50	26.37	92.0	266.0	A 87	No break
50	50	14.98	83.0	293.0	A 87	No break
50	50	26.37	142.0	186.0	D 36	23.6
50	50	14.98	139.0	206.0	D 35	26.0

* 50 phr dioctyl phthalate

Instrumentation

(I)   Automatic compression moulding machine CMP 30 from Nuchem , India.

(II) Xenostat Weatherometer 150 S.

Preparation of Blends

PVC grafted ethylene propylene ethylidene norbornene rubber was modified with thermal stabilizers (TBLS and DBLS) and lubricant (stearic acid) in 1.75 phr and 0.5 phr quantities. These modified grafts were mixed with plasticized polyvinyl chloride in 50:50 and 25:75 phr proportions. Melt mixed blends were extruded at 150-160°C to yield pellets. Pelletised blend was compression moulded in CMP 30 compression moulding machine and evaluated for its mechanical strength (Table 1).

Weather Resistance Studies

Weather resistance studies were carried out in Xenostat weatherometer. Compression moulded samples of blend in required shapes and sizes were clamped in the stands provided in the weatherometer. They were exposed there under artificial weathering conditions for 240, 360 and 720 h in mobile conditions. Samples were removed from the weatherometer from time to time and their hardness (Shore A/D), tensile strength at break, per cent elongation at break and impact strength were determined (Table 2). Per cent change in these properties before and after exposure were also calculated (Table 3).

Table 2 — EPDM rubber - polyvinyl chloride samples : exposed/unexposed

EPDM-PVC graft	PVC*	Chlorine content of graft (per cent)	Time of Exposure (h	Hardness (Shore A/D)		Tensile strength at break (kg/cm²)		Per cent elongation break	
				After exposure	Before exposure	After exposure	Before exposure	After exposure	Before exposure
50	50	26.37	720	A 87.0	A 87.6	84.0	92.0	265.0	266.0
50	50	14.98	720	A 85.1	A 85.4	77.0	83.0	289.0	293.0
25	50	26.37	720	D 34.0	D 36.0	128.0	142.0	166.0	186.0
25	50	14.98	720	D 27.0	D 34.2	126.0	139.0	182.0	206.0
0	100	--	240	D 60.0	D 67.7	139.0	165.0	132.0	170.0

* 50 phr Dioctyl phthalate

Table 3 — Per cent changes after exposure

EPDM-PVC Graft phr	PVC*	Chlorine content of graft (per cent)	Time of exposure (hours)	Hardness (Shore A/D)	Tensile strength break at kg/cm²	Per cent elongation at break
50	50	26.37	720	0.34	8.6	0.3
50	50	14.98	720	0.35	7.2	1.36
25	75	26.37	720	6.5	9.8	10.0
25	75	14.98	720	5.5	9.1	11.6
0	100	--	240	11.3	15.3	22.0

The weatherometer was maintained at constant temperature (47 ± 3°C and relative humidity conditions (65 per cent). Mobility of stands provided better exposure conditions for samples.

Results and Discussion

EPDM rubber - PVC blend studies carried out here can be divided into two groups : (i) 50:50 phr blends and (ii) 75:25 phr blends.

(i) contained grafted rubber and polyvinyl chloride in same proportion, whereas (ii) contained higher proportion of plasticized PVC. Various mechanical properties; tensile strength at break, impact strength, hardness (shore A/D) and per cent elongation at break were determined for both the blend categories. Plasticization level of polyvinyl chloride was also varied in order to study the variation effects, if any. Table 2 records the mechanical property values studied over here both before and after exposure to UV light. Per cent fall in these properties after exposure are tabulated in Table 3. It is obvious from the Table 2 and 3 that the blend with higher EPDM content has better weather resistance as compared to the blend having higher proportion of polyvinyl tensile strength at break and per cent elongation at break values are 0.34 per cent and 6.5 per cent, 8.6 per cent and 9.8 per cent and 0.3 per cent and 10 per cent for 50:50 and 75:25 blends respectively. These differences in the values can be explained in terms of the good weather resistance of EPDM rubber. Polyvinyl chloride on the other hand, has shown 11.3, 15.3 and 22 per cent fall in hardness, tensile strength at break and per cent elongation at break after 240 h of exposure. For a balanced set of properties, mechanical strength as well as resistance to ozone, 50:50 blend was concluded to be the most suitable.

Conclusion

Ethylene-propylene ethylidene norbornene rubber blends with polyvinyl chloride have weather resistance of high degree. These blends possess high Izod impact strength too. Mechanical strength on the

whole is moderately good. The blends find use as laminates on EDPM rubber surfaces and in outdoor automobile applications.

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BOOK REVIEWS

Industrial Dynamics and Fragmented Labour Market: Construction Firms and Labourers in India, by Theo van der Loop (Sage Publications, New Delhi) 1996, pp 452, Price: Rs 525 (h b).
[ISBN 81 7036 491 4 (hb)]

The book is the second in the series "Livelihood and Environment"; a long time research programme of the faculty of Environmental Studies, University of Amsterdam, The Netherlands. The present book is the result of the author's research on construction industry in India during 1985-89.

The study depicts, in painstaking details, the production system and labour system of construction industry in India with the help of case studies done in two South Indian cities, namely Salem and Vellore. The study addresses the following four major issues:

(a) Small scale enterprises and its ability to generate income and employment for poverty alleviation;

(b) Phenomenon of informalisation of production system;

(c) Mechanism of "Conservation and Dissolution" in the process of transformation towards capitalist modes of production; and

(d) Issues of flexible specialization.

These issues have different heredity: from a shade of Marxian stable to modern technology and innovation management and prophecies of ILO and World Bank for the third world/under- developed/developing countries.

Any one of these issues legitimately deserves a book of 450 pages. The novelty of the book under review is that it attempts to deal with all the above mentioned issues including some more in a single book. As a result the book puts forward a challenging task to readers to continuously tune and retune the reader's mind in the maze of issues dealt in.

Author's main focus, however, appears to be exploitation of labour and various methods in the production process and labour systems by which exploitation is strengthened. He has tried to present a counter proposition to current academic and policy emphasis on small scale enterprises and informalisation of production system.

Author has seen informalisation as a part of the process of transformation towards capitalism through the process of conservation and dissolution of pre-capitalist mode of production. The study tries to bring out how informalisation helps fragmentation of labour market and retains pre-capitalist social and economic characteristics for creating a stable exploitative edifice.

In doing so the author has picked up debate with neoclassical economic theories. Although not categorically mentioned, author appears to be trying to erect a Marxian foundation against neo- classical approach. This, however, remains the weakest aspect of otherwise meticulous case study of the construction industry of India.

Among many reservations about his so-called theoretical discussion, a few are: (a) Present debate (at academic and policy level) on informalisation *vis-a-vis* Fordist mass production refers to a system of full fledged capitalist production. How the same can be confronted with cases taken from a system which at best can be called "in transition" towards capitalism?, (b) Are labourers less exploited in a fully developed capitalist system? Even within typical Marxist scheme, the concern is not degree of exploitation but unleashment of productive forces, (c) Marx tried to construct a homogeneous category of "Labour Force" through the machination of capitalist production system where surplus generator and surplus appropriator come face to face and religion, cast, creed, etc.,are thrown away as pre- capitalist vices. Fragmentation of a labour force through informalisation of the production system is a different theoretical premise from a production system with pre-capitalist form of fragmented labour force.

Author's case of construction industry in India does not merit a debate with contemporary phenomenon of informalisation in capitalist system. The misplaced debate has marred the otherwise in-depth empirical

insight into a most neglected section of the industrial activities and its labour force. Empirical insight derived from the investigation is so dispersed over various debates that it becomes difficult to trace a connecting thread.

In fact, while many of the theoretical deliberations could be called redundant, the treasure of the book is in the empirical findings on sub-constructing and labour system. Even in those sections, a straight forward presentation of empirical findings unadulterated by theoretical profundity would have been much better for the readers. The problem with the book is evident right at the beginning where on page 19 the author writes, "To be sure, the latter type of research (policy oriented research) is quite essential, but 'purely scientific' research is just as important". Clearly the author is bitten by the "Scientific" bug.

It is not clear that what does author mean by being "scientific". And how has he ensured himself that his theoretical venture is "scientific" enough?

Similarly, arriving at the end of the book (Chapter 11: Theoretical Implications and Policy Considerations) author's emphasis on entire production system including inter-firm relations and its interaction with the labour system (particularly, an autonomous impact of the survival strategy of labour force) has strong methodological implications for such empirical studies.

Importance of this issue, however, stands on its own without the wisdom of "Conservation-Dissolution" process or the process of informalisation in a capitalist production system.

Besides this, other conclusions about the future (in section 11.2) are minor in nature. Author's final words on flexible specialization in construction industry are again misplaced. Caste, religion, etc., play a very critical role in author's understanding of the production and labour system in the construction industry, in India. This demands an in-depth understanding of Indian caste system with all its anthropological and sociological dimensions. Author has raised a question regarding co-operation of different work groups when they are structurally divided along caste lines. A little more in-depth knowledge about caste system would have helped understanding that such co-operation is not impossible, rather quite common along the caste lines.

In short section on "policy considerations" author has expressed reservation about policy prescriptions, favouring government's efforts to promote small scale enterprise. Does the author suggest that small scale enterprises should not be promoted by governments? Well, the author refrains himself from making any such direct policy suggestions. Is it because of his lack of confidence on his own study?

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Technological Collaboration — The Dynamics of Cooperation in Industrial Innovation, edited by Rod Coombs, Albert Richards, Pier Paolo Saviotti and Vivien Walsh (Edward Elgar Publication, Cheltenham, UK) 1996, pp 232, Price: £ 49.95 (h b).
[ISBN 1 85898 235 9]

The importance of this book lies in effectively putting together the various views and perspectives on technological collaboration and networking. The present scenario of globalization has enhanced the formation of both formal and informal interactions amongst the actors of the innovation process like, firms, research institutions, Universities, resulting in the creation of complex networks. Associated with this Network formation are some important issues that need an in-depth analysis like why do firms go in for collaborations? What motivates collaborations? What is the nature of collaboration? In the present context of globalization what is the significance of multiple linkages and the resulting complex networks? What actually are these networks, are they collection of various individual collaborations or a more complex simultaneous interaction having several partners participating in it? These are some of the issues requiring an interdisciplinary approach to understand the complexity of the interactions. Normally, literature in economics had treated collaboration in terms of formal contract between the partners. 'Actor-network' theoretical framework where the emphasis is on the process of interactions among the actors is what sociologists have used to explain the collaborations and the complexity of the network. In *Evolutionary Economics, Networking* has been explained in terms of international competitiveness and spiraling cost and the associated risk factor. In this book, the multifaceted linkages amongst the various actors of the innovation process have been analysed and explanations have been provided beyond formal market transactions.

The book comprises 11 articles including the introduction. These articles could be broadly grouped into three categories: (1) Limitations of Transaction Cost Economics in understanding collaborations and Networking, (2) Technological collaborations in the 'actor-network' framework, (3) Why and how the networks are formed? what comprises the network and what actually are the result of this network?

Chesnais in his article has put across the view that the firm has a central role to play in resource generation and transformation of the same. He strongly argues that the firm cannot be treated as an alternate to the market as put forward by the scholars who analyse the cooperative alliances in the transaction cost framework. Similarly, Yamin in his article argues that strategic alliances cannot be explained in terms of markets and hierarchy. According to him, complex multifaceted linkages cannot be understood in terms of transaction cost, as it is not simply an addition of various collaborations. The networks, thus created are much more complex and dynamic. He further argues, that the strategic alliances are more for creating new knowledge, and the formation or the dissolution of a network depends to a large extent on the knowledge base of the partners and their ability in creating new knowledge. Leveque et al.; in their paper have elaborated upon the firms R&D activity and according to them the nature and type of cooperation depends upon the participating firms internal capabilities. They have dealt with cooperative linkages amongst the firms within the industrial R&D theory. They have also shown that sourcing of external R&D as a result of this cooperation is complementary to the internal R&D and cannot substitute it. They have also, like Chesnais, emphsised the role of firm as a unit. Transaction Cost Theory is largely being used by scholars to understand the organisational framework of collaborative linkages and hence, these three articles are very important because they have shown in their respective articles the limitations of Transaction Cost Theory to understand collaborative linkages in certain situations.

The 'actor-network' framework has been used for understanding network, according to which the actors' very existence is due to interactive relationships they have among themselves, resulting in the network formation. This is a dynamic process. Mangematin, in his article has examined this approach by taking the example where, firms have come together for the development of a technology. He has demonstrated that the level of trust among the partners and the form of technical product has an important link. In this case the linkages are with a purpose where the benefit of each of the partners is thought of in advance. A situation where the trust among the partners is low but the partners have come together for the development of a technology depending upon their technological capabilities, technology appears to be an important mode of coordination among the partners. Laredo and Mustar, in their article, have examined the EC programme to elucidate the complexity of the formal and informal linkages among the partners in the total innovation process. Under the 'actor -network' framework, all the actors being socially interactive, have shown that these interactions result in new modes of interactions and also creation of new relations. This, according to them, has resulted in the formation of 'technoeconomic-networks', and have been shown to be a new form of economic actor, encompassing the whole range of the innovation process. Both the articles have demonstrated the complexity of the network formation under the 'actor-network' framework.

Tylecote, in his article has shown that sociological factors to a large extent influence the nature and type of collaborations. By taking the cases of Japan, the UK and Germany he has shown how the sociological factors determine the orientation and priorities and hence, the variation in their collaborative interaction and network formation. Dodgson has explained the network formation in the context of learning process and in terms of the trust that the firms have with each other those results in shared learning. He has presented a review of theoretical understanding of learning and has discussed how and why the firms in competitive environment have adopted cooperative means.

Senker and Faulkner, have elaborated in their paper the role of tacit knowledge in the innovation process. By taking the examples of newly emerging technologies they have discussed the tacit knowledge exchange through personal networks. In high technology areas, informal sharing of knowledge among the competitors through cooperative networking seem to show an increasing trend. Similarly, Steward and Conway, in their paper have shown the importance of informal interactions and the emergence of new networks. They have also shown how these informal interactions contribute to the innovation process.

Niosi has explained the networking and collaboration among the firms in the context of a shift in the technoeconomic paradigm caused by information technology. He suggests a certain organisational innovation to have taken place to accommodate and adjust to the technoeconomic paradigmatic shift. A new form of collaborations is emerging among competing firms because of cost escalation and risk associated with the new and emerging high tech areas. He has tried to trace out an evolutionary pattern in the collaboration and strategic behaviour of firms by taking the case of Canada.

It is a timely book dealing with the important issues and complexity associated with collaborations and the resulting network formation. The book will provide important insights to the students and researchers of industrial economics, innovation management, and organisation studies.

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Cooperative Management of Natural Resources, extracted by Kartar Singh and Vishwa Ballabh (Sage Publications Pvt Ltd, New Delhi 110048) 1996, pp271, Price: Rs 350 (Cloth)
[ISBN 81 7036 5457 (India, h b)]

This book arising out of deliberations at a workshop on 'Cooperatives in Natural Resource Management', organised by the Institute of Rural Management, Anand (IRMA), Gujarat, provides a rich reservoir of information and data on the role of cooperatives in ensuring judicious use of natural resources for sustainable development. It is a matter of common knowledge and concern that the practices currently being adopted in India for exploiting her natural resources are in most cases, highly wasteful. Various presentations included in this book describing alternative systems of management of natural resources suggested by eminent experts are quite refreshing. Some case studies, covering aspects like wastelands, forests, ground water, surface water, salt and fisheries have enhanced the value of the book by their inclusion.

The book at the outset examines the rationale of cooperative/collective management of natural resources and traces the evolution of natural resources management cooperative societies (NRMCS) and then goes on to present an overview of the contents of fourteen presentations on natural resources management. Several policy instruments aimed at achieving efficiency and equity in the use of both surface and ground water in India have been suggested. Need for a strong political will at all levels to promote cooperativisation of common pool resources in the country, and to motivate local people / individuals to take collective action in managing natural resources has been emphasized. Recognizing that NGOs have requisite technical expertise and financial resources, it is emphasized that they must play an important role as catalysts in organising, educating, and training natural resource users.

Chapter 2 deals with the activities of *'Vatra Tree Growers Cooperative Society'*. Though various models of cooperatives are operative in India, the *'Vatra Tree Growers, Cooperative Society'* has made a pioneering contribution towards improving the sustainable levels of income of the villagers, particularly the poor by : (a) restoring the productivity of wastelands, (b) planning to distribute the benefits in an equitable manner, and (c) enabling the local people, through participation, education and training, to manage their own natural resources and development. Need is emphasized for the society, in general, to address these issues and resolve them satisfactorily.

Chapter 3 gives details of a case study from Orissa relating to people's participation in organizing and managing *'Tree Growers Cooperative Societies'*. The study has revealed that peoples' participation was high in the old tree growers cooperative societies and relativity low in societies of relatively recent origin. It is felt that local peoples' participation could be increased once the cooperative society starts generating confidence in the people in the areas where there is utility of cooperative management.

The case study from Himachal Pradesh, included in Chapter 4, describes the responsibilities and activities of *'Village Cooperative Forest Societies'*. An overview of the evolution and functioning of these societies is given. It is stressed that local people must cooperate in protecting natural forests if they are granted exclusive property rights. It is suggested that the role of the government should be confined to providing legitimacy and technical and financial support to the forest cooperatives.

Among the other important topics covered are: *'Cooperative Management of Minor Forest Products in*

Madhya Pradesh, Salt Miners', Cooperatives in Rann of Kachchh in Gujarat, Cooperative Lift Irrigation Societies in Western Maharashtra, Cooperative Management of Reservoir Fisheries in Himachal Pradesh, and Captain Bhery Fishermen's Cooperative Society in West Bengal.

Among the various alternative systems or regimes projected for effective management of natural resources, the ones that are prominent are privatisation, nationalization, and cooperativisation. In the opinion of the editors, cooperative management of natural resources holds the highest promise as an instrument for achieving the goals of efficiency, sustainability, equity, and resource users' satisfaction if it is appropriately programmed.

An obvious lacuna of the book is the absence of views and suggestions from representatives of farming and artisan communities which constitute an important segment of users of natural resources. It is hoped that this aspect would be taken care of in future meets of this type.

On the whole the book is a useful compendium of information on different models of cooperatives engaged in natural resource management. It would be of value to economists, planners, NGOs and various governmental functionaries.

The book is well produced, but its high price could be a deterrent for its finding a place on the shelves of interested individual readers.

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SCI & TECHNOL UPDATE

Nobel Prizes 1996

Economics

Two microeconomic theorists, Prof William Vickrey (82), USA, Prof James Mirrlees (58), UK shared this year's economics Nobel Prize explain how the lack of adequate information can still help shaping modern business decisions. Prof Vickrey is an emeritus economist at Columbia University in New York. With profound regrets it is stated that Prof Vickery died recently through an automobile accident. Prof Mirrlees is an political economist at Cambridge University, London.

Basically their area of research concerns what economist call asymmetric information referring to when both sides do not have the same facts. The buyer of a house or a used car, for example, doesn't have all the information the seller does. Without the same facts. The seller has an advantage over the buyer, who must spend time and money to learn more.

Although their separate studies of (late) Prof Vickrey and Mirrlees focused on relatively specific areas such as actions and subway fares, their work has led to better understanding of economic activity ranging from insurance and credit markets to tax systems, job markets etc.

One of the most important and liveliest areas of economic research in recent years addresses the situation where decision makers have different and even conflicting information, which is an important characteristic of asymmetric information.

Incomplete and asymmetrically distributed information has fundamental consequences, particularly in

(Late) Prof W Vickrey   Prof. J Mirrlees

the sense that an informational advantage can often be exploited strategically. Research on the economics of information has therefore focussed on the question of how contracts and institutions can be designed to handle different incentive and control problems. This has generated a better understanding of insurance markets, credit markets, auctions, the internal organisations of firms, wage forms, tax system, social insurance, competitive conditions, political institutions, etc.

An essential part of (late) Dr. Vickrey's research concerns the properties of different types of auctions, and how they can best be designed so as to generate economic efficiency. His endeavours have provided the basis for a lively field of research which, more recently, has also been extended to practical applications such as auctions of treasury bonds and band spectrum licences. In the late 1940s, Dr Vickrey also formulated a model indicating how income-taxation can be designed to attain a balance between efficiency and equity. A quarter of century later, interest in this model was renewed when Dr James Mirrlees found a more thorough solution to the problems associated with optimal income taxes. Mr Mirrlees soon realized that this method could also be applied to many other similar problems like moral hazards. ☐

RS

Physics

Three American cryogenic physicists, Prof David M Lee (65) and Robert C. Richardson (61) Cornell University, Ithaca (NY) and Douglas D. Osheroff (52), Stanford University, Stanford, California have shared this year's physics Nobel Prize, for their pioneering discovery (1971) of superfluidity in liquid Helium-3; this occurs only at temperatures below 2mK, whereas the normal liq He^4 (Bose-Finstein condensate) becomes superfluid at a relatively higher temperature (2K).

The liquid-helium system,s viz, He^4,He^3 and mixtures of these liquids have been the most extensively investigated for the past 4 decades or so, ever since
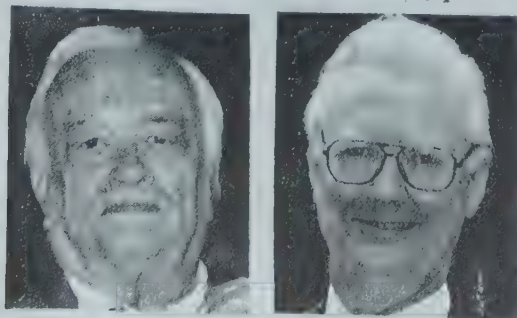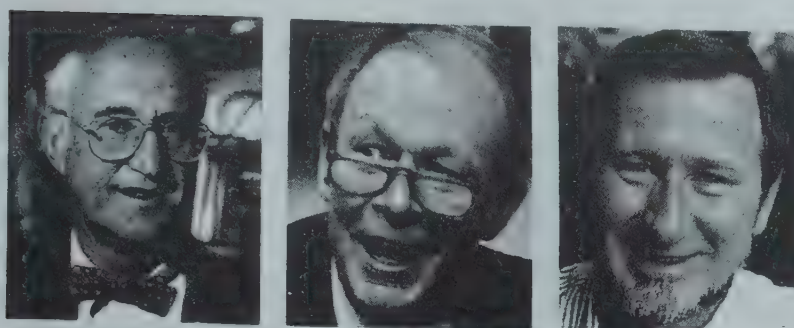
Prof. D M Lee   Prof. R C Richardson   Prof. D.D. Osheroff

Kammerling Onnes, father of low temperature of physics liquefied helium in 1908. The primary reason being that the liquid helium (in all its phases) refuses to be solidified unlike other noble gases, even in the vicinity of absolute zero, unless tremendous pressures are applied exceeding 20-25 atmospheres. Since at these temperatures, below a few Kelvin, the random thermal agitation is mitigated and the liquids exhibit quantum behaviour prominently.

Basically superfluidity, is a special state of matter which can flow without viscosity; however characterization of the superfluidity in He^4 and He^3 is fundamentally different, because the former is a boson (integral spin) consequently can easily become superfluid, at about 2K as first detected in 1938. Fundamentally, He^3 has much larger zero point thermal energy than

He^4. All attempts, since then (till the work in 1972 at Cornell by the trio winning the 1996 Nobel) to transform liq He^3 to superfluid state failed. This is because He^3 is basically a fermion (half-integer spin) can form a boson, only by pairing with another He^3 atom, through magnetic ordering. Such pair formation could occur only at very low temperatures (below 1K) which is generally difficult to maintain.

Staying together at Cornell during early 70s at Cornell, Profs Lee, Richardson and Osheroff, discovered superfluidity in He^3 rather accidentally. They were then studying the high pressure properties of solid Helium-3. In particular in the experimental cell (Fig 1), they found liq He^3 co-existed with solid helium, as a refrigerant; then in 1972 they conducted the process of "compressional cooling". This is based on the fact that when a mixture of liquid and solid helium 3 is compressed, some of the liquid is converted into a solid and the temperature of the mixture drops. Furthermore, near 2.7mK they detected a 'glitch' in P vs T on the melting curve of solid He^3, which suggested a possible
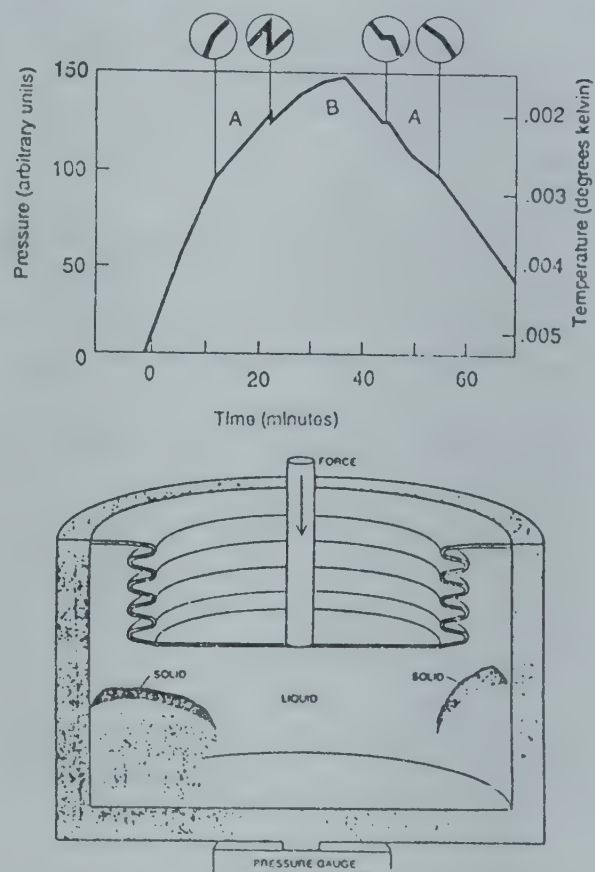
Fig.1 — Cell for compressional cooling of solid-liquid He phases; phase transition under pressure depicted in insert diagram

modification in the phase of helium liquid, perhaps onset of superfluidity (insert in Fig. 1). The superfluid transition in helium 3 was first observed at a temperature of .0027 degrees above absolute zero, which is about 1,000 times colder than the superfluid transition temperature of helium 4. (Strangely enough superfluid temperature of 2.7 mK was much higher than the theoretical prediction). Subsequent mechanical experiments at Helsinki on the damping of an oscillating strings in He^3 confirmed superfluidity.

From the time superfluid helium 3 was discovered it has been apparent that it is an even stranger substance than superfluid helium 4 or. The very first experiments revealed not one superfluid transition but two, taking place at 0027 and 0021 degrees K and at a pressure 34

atmospheres. The two new phases that appear as the liquid is cooled through these temperatures have been named He^3-A and He^3-B. When the cooling is done in a magnetic field, still another phase, He^3-A_1, appears in a narrow range of temperatures between the A phase and the normal liquid. Thus in a small region of the phase diagram helium 3 exists in five distinct phases: the solid, the normal liquid and three kinds of super-fluid. The multiplicity of distinct superfluid phases in helium 3 and several other properties of the liquid set it apart not only from ordinary liquids but also from helium 4 and superconductors.

The distinction between three different phases of He^3 on the basis of different magnetic or temperature conditions led to new results recently; phase A is highly anisotropic like a liquid crystal unlike liquid He^4. This property was exploited in the experiment of vortices set into motion inside a He^3 superfluid, something that happened during early big-bang Universe (!). Another one revealed by Prof Osheroff *et al.* on the basis of earlier theory of Leggett (Illinois) that a piecemeal transition of A-phase into B-phase He^3 could result by supposing droplets of latter nucleated within the super-cooled A-phase. In particular, they synthesized viz process nicknamed 'Alaska baking' of B-phase nuclea-tion from A-phase by initiation through cosmic rays. In these experiments, neutrino-induced nuclear reac-tions heated the He^3 sample and generated vortices that mimic cosmic strings !

Like He^4-superfluid, He^3-superfluid has several im-portant applications esp. as a probe in condensed matter physics. To cite an example, the magnetization of a thin He^3-film is a sensitive probe of the geometry of the space in which it is supported, believed to be a fractal one.   ❑

                                                          RS

Chemistry

The Nobel Prize in Chemistry has been jointly awarded to two US scientists— Prof. Richard E Smal-ley and Prof. Robert F Curl (Jr)—and a British scien-tist—Prof. Harold W Kroto—for discovering a novel form of carbon that led to the development of a new field called 'Fullerene Chemistry'.

It was in 1985 when Prof. Croto of the University of Sussex, Brighton, UK, was studying the formation of long-chain carbon molecules in interstellar space along with Prof. Smalley, Prof. Curl and others at the Rice
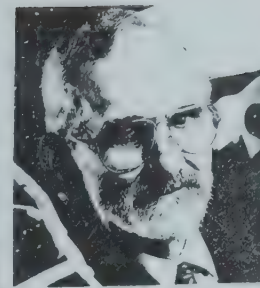
Prof. Richard E Smalley   Prof. Robert F Curl(Jr)

Prof. Harold W Kroto

University in Houston (USA) that the team discovered the presence of a superstable cluster of 60 carbon atoms in the vapours of laser-irradiated graphite in inert at-mosphere. This big monster of pure, solid carbon atoms was assigned a soccer-ball-like structure and was chris-tened as 'Buckminsterfullerene', and affectionately called as 'buckyball'. Later, with the discovery of more such molecules as C_{70}, C_{48}, C_{84}, etc., the group was termed as 'Fullerenes'. A large number of re-searchers—chemists, physicists, metallurgists, phar-maceutical chemists, technologists—are studying these big clusters of carbon atoms from various angles. The high cost of production of C_{60} is, however, a great hindrance in making it a molecule of common usage.

The group will receive 7.4 million kroner ($ 1.12 millions) as the prize money this year.   ❑

                                                         BSA

Physiology and Medicine

Profs Peter C Doherty (63) from USA and Rolf Zinkernagel (58) from Switzerland have been awarded this year's Nobel Prize for physiology and medicine for
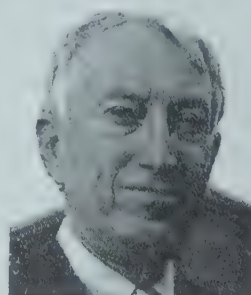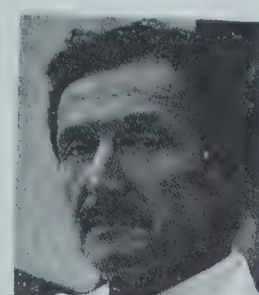
Prof C. Doherty   R. Zinkernagel

their discovery during 70s as to how the immune system recognizes virus-infected cells. The Nobel citation mentions that their work is of fundamental importance in clinical medicine, especially in the treatment of dreaded or chronic inflammations and in some types of cancer. Furthermore their work has led to a proper understanding of the general mechanisms used by the cellular immune system to recognize both foreign micro-organisms and self molecules.

Prof Doherty is concurrently with St Jude Children's Research Hospital and University of Tennessee in Memphis, Tennessee (USA) Prof Zinkernagel is from the Institute for Experimental Immunology, Zurich University, Zurich (Switzerland). Moving to Canberra's (Australia) John Curtis School of Medical Research in 1973, they commenced their researches on cell immunology together. In particular, they soon devised means to distinguish between antibody-mediated and cell-mediated immunity. They have also investigated upon the immune response against invading micro organisms with a view to diminish the effects of autoimmune reactions in rheumatic ailments, multiple sclerosis and in some forms of diabetes.

Their early investigations comprised immune response of mice to viruses and they found that white blood cells (*lymphocytes*) must recognize both the virus and certain self-molecules — the so- called major histocompatibility antigens — in order to kill the virus-infected cells.

The immune system consists of different kinds of white blood cells, including T- and B- lymphocytes whose common function is to protect the individual against infections by means of eliminating invading micro-organisms and infected cells. At the same time they must avoid damaging the own organism. What is required is a well-developed recognition system that enables lymphocytes to distinguish between on the one hand micro- organisms and infected cells, and on the other, the individual's normal cells. In addition. the recognition system must be able to determine when white blood cells with a capacity to kill should be activated.

It was known that antibodies that are produced by B-lymphocytes are able to recognize and eliminate certain micro-organisms, particularly bacteria. Far less was known prior to their investigations about recognition mechanisms in the cellular immune system, for
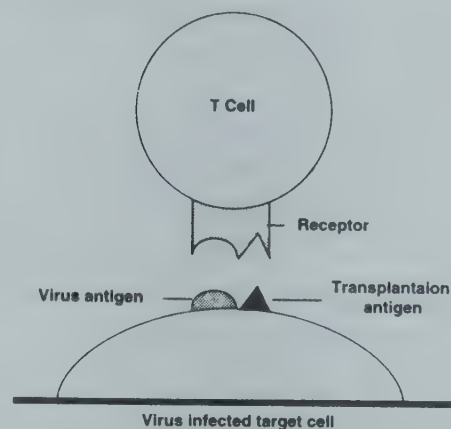
Fig 1 — Schematic diagram of identification of T-cell lymphocyte of the virus-infected cell

instance in conjunction with the killing of virus-infected cells by T-lymphocytes (Fig.1). One area where cellular immunity had previously been studied in some detail was, however, transplantation biology.

In the Nobel laureate's study infected mice developed killer T- lymphocytes, which in a test-tube could kill virus-infected cells. But there was an unexpected discovery: the T-lymphocytes, even though they were reactive against that very virus, were not able to kill virus-infected cells from another strain of mice. What decided whether or not a cell was eliminated by these killer lymphocytes was not only if they were if they were infected with the virus, but also if they carried the 'correct' variant of histocompatibility antigens, those of the infected mouse itself. Their findings, which were published in *Nature* (1974) demonstrated the conditions needed for proper identification of immune response of T-cell.   ❑

RS

Structural design of tubular trusses using knowledge- based expert system

Computers are ideally suited to store bulky data of various possible ways of achieving optimum solutions by means of what are known as expert systems.

An EPSRC-funded project at Nottingham University and UMIST has developed an Integrated Design System using an embedded knowledge-based expert system that enable designers to carry out appraisals of various options for designing tubular trusses. The system enables designers to obtain an economic solution that can simultaneously consider both the structural design and the fabrication stages. Tubular trusses were chosen as the illustrative structural form initially for their study since they are particularly sensitive in terms

of production costs to decisions taken at various stages of the design process.

The IDS enables the designers to analyze, design and estimate the cost of the manufacture of a truss using a fabrication cost model The cost model is implemented so that it eases the comparison of alternative details, and the evaluation of the consequences of design decisions on cost.

The IDS highlights features that adversely affect fabrication cost, unsuitable design options, and recommends suitable modifications.

The module informs designers of the adequacy of a given joint and, where applicable, advises on means of improving the detail to alleviate expensive fabrication operations and, at the same time, ensuring adequate strength.

The working of IDS contrasts with the conventional process that in many cases yields solutions with significantly higher overall cost of construction. The IDS, with minimal additional effort at the design stage, can avoid esoteric solutions and ensure the production of workable and competitive designs from both the structural and fabrication viewpoints.

This project has successfully tested the feasibility of using information technology, engineering knowledge and cost data, to develop a tool that can aid practically in the re-engineering of the design process by allowing the simultaneous consideration of two main stages of the construction process.

Future work will extend this approach to include other construction stages such as transportation and erection and will broaden the structural forms considered.

For further information contact: David Nethercot, Department of Civil Engineering, University of Nottingham (0115 951 3904; fax 0115 951 3898; Email: david.nethercot @ nottingham.ac.uk) [*Bldg Civil Eng Res Focus*, UK, **No. 26**, August 1996, p. 2].   ❑

DSRM

Software for obtaining picture more quickly developed

Kodak has developed a new file format that builds on technology already used in Kodak's Photo CD system. It makes file handling at least ten-fold faster on a typical PC. Kodak has recently collaborated with Hewlett-Packard, Microsoft a company named Live Picture to promote the system called FlashPix. Apple, IBM, Fuji, Cannon and Corel will support from outside.

A single FlashPix file stores the same image in a hierarchy of resolutions, ranging from an accurate representation of the colour original to a coarse monochrome image just 64 pixels square. To save bit space, each version is compressed using the established JPEG standard.

When manipulating the file, the PC automatically uses the level of image quality best suited to the task in hand. For example, when pictures are made available on the Internet, users can opt first for a rapid display of a thumbnail image, and click again for a higher-resolution version of the same image if they wish to. Similarly, newspaper layout artist can quickly position a coarse image on a page before pulling in the full resolution version.

Each image, at each resolution, is divided into rectangular files. This lets the PC zoom in and work on a small area without having to process the whole file.

When changes are made to an image, FlashPix stores them as "viewing parameter" instructions. Instructions created quickly on a low-resolution image are only applied to the high-resolution version when all the work is done.

The full technical specification for FlashPix was released recently on the Internet, free for any company to use without having to pay royalties.

The finished FlashPix software is promised in 1997 by Kodak [*New Sci*, **150** (2035) (1996) p.22].   ❑

HKK

3D-video technology developed at Stanford

Displaying of three-dimensional objects in fluorescent glass dates back to 60s, but due to severe material problems, the resolution and image intensities are not good for possible commercial exploitation. But now Prof Hesselink and his graduate student Ms Elizabeth Downing at the Electric Engineering Dept, Stanford University, Stanford (USA) have developed a versatile and novel 3d-imaging technology inside a clear glass of the size of a sugar cube. The cube is located at the centre of a square device Cof size 30 cm^2, holding miniature lasers, scanners, prototype components, etc.

The video display of the device can generate 3d-colour images inside a cube of fluorescent glass. In particular they demonstrated the generation of a 'wobbled' 3d-ring of neon-pink light with characteristic twisting and dancing (!).

The display's characteristics make it useful for: medical imaging; virtual prototyping of products using computer-aided design tools; and scientific visualization of large, complex systems like turbulent airflow around aircraft or water flow around submarines.

Starting with the simplest mode of stereo pairs of slightly different perspective, several 3d-image display techniques are currently in vogue. The video equivalent pairs each eye with its own video screen showing a slightly different view to create stereo images. Another approach to 3-D is to stack a number of two-dimensional images on different planes, a process used with medical CATscan data. A third technique is holography, which stores three-dimensional information in invisible patterns on a film. When this film is illuminated by laser light, three- dimensional images appear to a viewer looking through the film. But all these technologies have some limitations or the other, making the displays highly localized. The new development at Stanford avoids these short-comings in a novel fashion.

Ms Downing got the basic idea of the new device from the early unsuccessful attempts during 70s by a team at Battelle Memorial Institute at Columbus (Ohio); this was partly because efficient semiconductor lasers or good quality fluorescent glasses were not available then. Now with quality components available, the Stanford group has worked out a novel device which in fact produces an image that is drawn in three dimensions (not actual 3d but in 'virtual reality'). Hence there are no longer restrictions on the number of people who can visualize the display *albeit* a truly commercial proposition. Also the images are emissive, they glow-rather than reflective, so they can be seen easily in ordinary room light.

The fluorescent glass display is based on a scientific principle called "upconversion". Certain atoms in the rare earth family emit visible light when struck in rapid succession by two infrared laser beams of slightly different wavelengths Different kinds of atoms emit different colours of light when stimulated in this fashion. To make a display, small amounts of these atoms

are mixed (doped) into the glass as impurities. A simple way for upconversion is to use clear plastic cubes filled with rare-earth crystals. When the two infrared laser beams, which are invisible to the naked eye, are directed through the glass, a point of visible light is created where the two beams intersect.

For the model display, Stanford team used surplus scanners from optical disk players to scan the two laser beams vertically, horizontally, and backward and forward through the volume of the cube. Visible images are produced by controlling the points where the two beams intersect. In this fashion one can easily successfully create 3d- wire figures, surfaces and simple solid shapes. The surfaces formed, however, are transparent, not opaque like those of most common objects. This could be a drawback for some applications, like television or desktop computer displays, but an advantage for others, like medical imaging or scientific simulation.

Another potential drawback for some uses is the fact that it takes 500 times as much data to construct a three-dimensional object as it does to draw the same object in only two dimensions. In a separate project, Prof. Hesselink has been working on holographic storage technology that has the high-speed data transfer capability needed to drive such a display.

The 3d technology can generate color images by employing what Prof. Hesselink refers to as "the Trinitron approach" Impurities that create red, green and blue colors are mixed into the glass in separate layers that are very close together. When the laser beams stimulate adjacent layers at nearly the same time, the different colors fuse into a single colored dot. The current testbed device consists of three relatively thick layers, one for each color. So a pink object appears in front of a green object that appears in front of a blue object. An actual display, however, would consist of thousands of groupings of red, green and blue layers so that 3-D objects of any color could be created.

In retrospect, it must be mentioned that although the Stanford 3d-display project got adequate funding to the tune of 4m dollars from Navy and Dept of Defence through center for Non linear optical Materials during various stages, it was not all smooth sailing for Ms Downing. Thus the initial funding allowed Downing to determine the proper glass mixtures to use and to test them with table-top-sized research lasers. By the time

she was ready to build a prototype using much smaller semiconductor lasers, however, she had nearly run out of money. In response to her request, SDL Corp. in San Jose furnished without charge the diode lasers and some of the other electronics that were required.

Undoubtedly medical imaging is apparently the most natural application for the new display technology. Currently, MRI, CATscans and ultrasound produce complex 3d images that are studied by stacking a series of flat pictures. The practitioners prefer transparent images because they do not hide any of the features. Moreover, the medical benefits of this improved display technology are likely to be great enough to pay for its expense, she added. It has been calculated that it would cost about $80,000 to make a prototype 10-inch display of this type [*Stanford News* (Stanford University Press, Stanford) 27 Aug 1996].   ❑

RS

Stabilization of microchips with deuterium for longer life

Replacing hydrogen with deuterium in the processing of silicon semiconductor chips could significantly increase the operational lifetime of the chips. The application, discovered by two electrical engineering professors may be the first use of deuterium as an industrial processing chemical.

Karl Hess and Joseph W. Lyding are professors of electrical and computer engineering at the university of Illinois, Urbana- Champaign and at the Beckman Institute for Advanced Science & Technology.

The deterioration that occurs in semiconductor transistors as they age is believed to be caused by the effects of "hot" electrons with energies in the range of 1 to 5 eV, the researchers explain. As these electrons pass through the Si/SiO_2 interfacial region during the transistor's operation, they stimulate desorption of chemisorbed hydrogen. The hydrogen is adsorbed as the semiconductor wafers are processed during a sintering step in a hydrogen atmosphere. The hydrogen improves the function of the semiconductor devices by serving as a passivating agent at this interface.

The use of hydrogen for annealing and passivating microchip surfaces has been adequate for computer technology so far. However, as the industry moves deeper into nanotechnology, devices will become smaller and be driven harder. They will need to be more robust and have longer lifetimes.

Lyding had previously used a scanning tunneling microscope (STM) to stimulate hydrogen desorption from silicon surface. He found that deuterium was about 100 times more difficult to remove from this surface than hydrogen. In discussing these results with Hess, the two realized that changing from hydrogen to deuterium might retard transistor aging without changing the operative chemistry at the surface.

The Illinois researchers obtained semiconductor wafers from Isik Kizilyalli, a research engineer at Lucent Bell Laboratories in Orlando, Fla, which they sintered in a deuterium atmosphere and returned to Kizilyalli for electrical stress tests. In tests of about 80 samples, Kizilyalli found the hydrogen and deuterium devices began with identical electrical characteristics, but the ones passivated with deuterium had operational lifetimes from 10 to 50 times longer than those passivated with hydrogen.

Lyding's STM experiments suggest that a large isotope effect may be part of the reason deuterium treatment extends semiconductor lifetimes. High-energy electrons may cause some of the silicon/hydrogen (or silicon/deuterium) assemblies to assume an antibonding state, which produces a force that accelerates hydrogen away from the silicon surface. The acceleration is much lower for deuterium because of its larger mass.

The complex processes associated with degradation of the interface are further complicated by interface reconstruction and defect chemistry. Thus, the full explanation of the effect may be more complicated. This is the first example of deuterium being used as a process chemical. At this stage of development, it appears that a simple exchange of deuterium for hydrogen is all that is required. No special equipment is necessary. [*Chem Eng News*, **74** (12) (1996) 25].   ❑

Dashboard computer to cut down road accidents

A dashboard computer could soon help motorists improve their driving skills. Its developers at the University of Groningen in the Netherlands claim their system can coach drivers in the most demanding traffic conditions.

The Generic Intelligent Driver Support system generates visual and voice messages to help the driver

anticipate and react to road hazards. The Dutch researchers hope that automated supervision of newly qualified drivers will help cut down on the number of road accidents.

The computerized heart of the GIDS system is split into two modules. The Analyst/Planner unit uses information from electronic sensors located around the vehicle to build a picture of what the driver is doing. The computer then compares this with what it thinks the driver should be doing and offers corrective advice. For example, traffic signs could be equipped with passive tags that give the sensors relevant information, such as speed limits.

GIDS combines global positioning system receivers with an internal map to determine the car's speed and position relative to features such as crossroads and other junctions. It also incorporates a collision avoidance system, similar to those used in aircraft, to monitor traffic. If the motorist is driving too close to the vehicle in front, a pressure system connected to the accelerator allows GIDS to increase the counterforce on the pedal and make the driver slow down.

The system's messages are prioritized by the Dialogue Control module, depending on the driver's workload.

The Traffic Research Centre of the university evaluated the GIDS system on a car using an active radar-based object detection system developed by the British arm of Phillips. The results indicate that GIDS reduces the average speed and rate of deceleration caused by slamming the brakes on. [*New Sci*, **149** (2021) (1996) 25]. ◻

Monitor with digital features

Phillips company has come out with a new generation of computer monitor—Briallance 21, a monitor with digital features suited to the cyberspace.

In the new monitor, for each representable pixel there is a separate microprocessor control for all three video amplifiers. In addition, the Cyberscreen technology compensates the influence of terrestrial magnetic field. A magnetic sensor determines the various variations of magnetic fields and leads two magnetic coils all around the tubes in order to create two opposing magnetic fields.

The monitor allows the user to adjust the display performance according to his requirement. The user can set the correct colour temperature or equalize any variations by feeding these commands using the PF keyboard which are communicated to the monitor via an in-built RS 232 interface. The user can have each and every colour balance with digital precision.

The monitor offers horizontal scanning frequencies upto 90 kHz. This guarantees a flicker-free screen. With autoscanning in the region of 30-90 kHz and automatic synchronization, the Brilliance 21 A supports resolutions of up to 1600 x 1280 pixels on High End PC's, Workstation, Mac II and Quadra computers, as also x-terminals. The Cyberscreen based on the standard MPR II corresponds to the ISO 9241/3 Standard. The TCO 92 version can be ordered optionally since the monitor is equipped with Power Down Management as per NUTEK.

The monitor is well suited for applications in the field of CAD/CAM, graphic design DTP, digital image processing, scientific model processing, etc. It contains an LCD display panel indicating the selected display mode and setting of the parameters. The data are displayed on a Flat Square Tube [*Prt Publshg*, July/Aug, 1996, p.31]. ◻

DSRM

Measurement of temperature with an infrared radiation thermometer

Infrared radiation thermometers have opened new vistas for industrial temperature measurements and control. IR thermometers give practically instantaneous readings of temperature of any surface upto 3000°C. The radiation intensity of any surface depends not only on its temperature but also on its emissivity. Therefore, if a pyrometer is used to measure the temperature of hot surfaces, either the emissivity of the surface has to be known or it has to be increased artificially to the value 1 when the temperature is to be determined from a pyrometer reading. Otherwise an apparent temperature is read which does not agree with the true temperature. In view of the industrial importance, the Testing & Calibration Cente, NPL, New Delhi has undertaken calibration of IR thermometers.

Since most of the hot objects do not behave like blackbody radiators, emissivity compensation is necessary to measure the actual temperature by an IR thermometer. It can be done by properly adjusting the

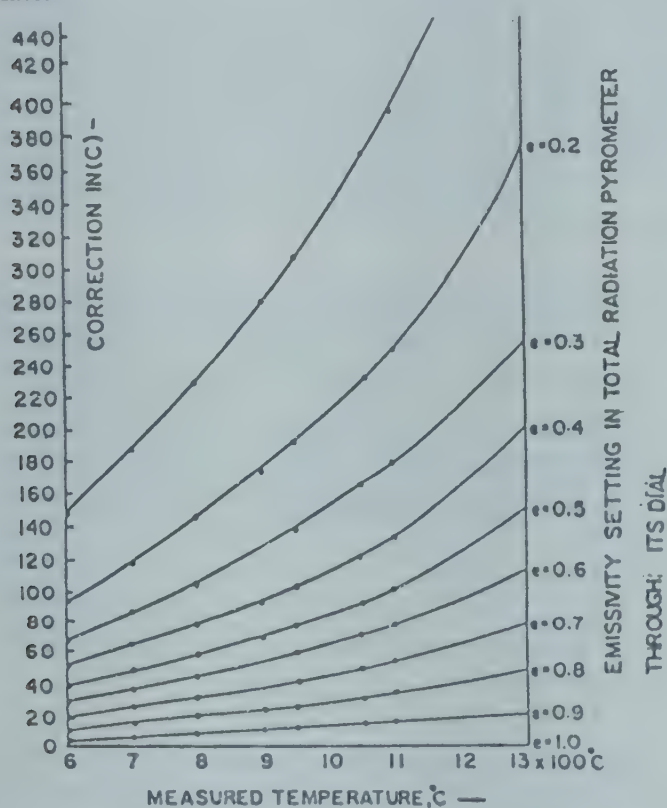Fig. 1 — Setup for calibration of pyrometer against blackbody radiator

Fig. 2 — Plot of pyrometer temperature variation with emissivity setting

emissivity setting of the pyrometer. If the emissivity is known, set the emissivity to the known value to measure the true temperature of surface in question. If emissivity is unknown, compare the measuring value using a thermocouple or the like and adjust the emissivity compensating setting of the pyrometer until the same value is obtained. Total radiation temperature is the temperature of a blackbody when it emits the same total radiation intensity as the surface towards which the pyrometer is directed. The relation between true temperature "T" and total temperature "T_t" is given by:-

$$\varepsilon_p \, \sigma T_1^{\,4} = \varepsilon_s \, \sigma \, T^4 \Rightarrow T = T_t \quad \text{if } \varepsilon_p = \varepsilon_s$$

where p is emissivity setting of pyrometer and s is emissivity of the surface.

Figure 1 shows the set up for calibration of IR thermometers ('Minolta Land') and Fig. 2 depicts the variation of temperature with emissivity setting of pyrometer.   ☐

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New large-pore silica zeolite prepared

Researchers at the University of Texas, Dallas, in collaboration with those at the CalTech, the University of Massachusetts, Amherst, and the University of Delaware, have developed a new high-silica zeolite containing several pores made up of 14 tetrahedrally coordinated silicon atoms. It is named the zeolite UTD-1 [Nature, 381 (1996) p. 295].

The large pores of UTD-1 are about 75 Å in diam. the calculated void volume of a unit cell is 900 cubic Å, which translates to 0.15 mL/g of material. This agrees with the experimentally determined volume from nitrogen adsorption.

UTD-1 was synthesized using bis (pentamethyl-cyclopentadienyl)- cobalt (III) hydroxide as a template. The pure silica version of UTD-1 was prepared by heating a mixture of the template and silica gel at 175°C for two days in an autoclave. Calcination in air at 550°C converted the template to cobalt oxide, which was removed with hydrochloric acid, followed by a water wash.

The concern was about UTD-1's stability. But despite the large pore openings, the thermal stability of the structure is remarkably high. Temperature dependent X-ray powder diffraction investigations show no loss in crystallinity below 1,000°C, even in a nitrogen atmosphere containing water vapour.

A form of UTD-1 that contains aluminium has Brönsted-acid sites with strength comparable to other high-silica zeolites, which permits a broad range of hydrocarbon reactions with UTD-1. Other catalytic elements such as titanium can also be incorporated into UTD-1's structure.

One of the attractions of large-pore zeolite catalysts is their utility for treating the progressively heavier crude-oil feedstocks being produced presently. One of the first applications that will probably be attempted

will be as an additive to fluid catalytic cracking operations to permit greater flexibility with the heavier crudes. Other applications might be hydrotreating catalysts and large molecule adsorbents. The large pore volumes may also permit use in reactions of steroids, molecules usually too large to fit into zeolite catalysts with smaller pore sizes [*Chem Eng News*, **74** (22) (1996) p.5].   ❑

<div align="right">HKK</div>

Use of manganese may cut lithium battery cost

A Robert Armstrong and Peter G Bruce at the University of St Andrews, Fife, Scotland, have prepared lithium manganese dioxide ($LiMnO_2$) that may substantially reduce the cost of making rechargeable lithium batteries. The material comprises layers of lithium, manganese, and oxygen ions [*Nature*, **381** (1996) p. 499].

$LiMnO_2$ is structurally analogous to the layered lithium cobalt dioxide ($LiCoO_2$) used as the positive electrode in commercial rechargeable lithium batteries.

Lithium ion batteries, also known as "lion" or "rocking-chair" batteries, are beginning to replace conventional nickel-cadmium or nickel-metal hydride batteries in portable electronic equipment such as laptop computers. Commercial lithium batteries have a $LiCoO_2$ cathode, a graphite-based anode, and an electrolyte containing lithium ions. Lithium ions shuttle back and forth between electrodes as a battery is discharged and recharged. Both electrodes intercalate, i.e., act as host for lithium ions.

The energy storage capacity of a rechargeable lithium battery being higher than conventional nickel-cadmium or nickel-metal hydride batteries so one can have smaller, lighter batteries which give the same power. But cobalt is relatively toxic and is quite expensive. On the other hand, manganese is less toxic and about 1% of the cost of cobalt.

Numerous groups are attempting to develop lithium manganese oxides to replace $LiCoO_2$. This new material is potentially attractive from that point of view. Related compounds have been made, but they have either contained water, which is not good for lithium batteries, or they are not direct analogs of the cobalt compound.

The ability to fabricate layered stoichiometric $LiMnO_2$ is an interesting advance. It has not been done

earlier and is an important step toward development of new intercalation structures for lithium ion batteries.

A prototype lithium battery using another manganese material, $LiMn_2O_4$, has been developed by several other groups and is at commercialization stage. $LiMn_2O_4$ is also an intercalation compound, but unlike $LiCoO_2$ and $LiMnO_2$, it does not have a layered structure.

It is reported that the charge capacity of $LiMnO_2$ compares well with that of both $LiCoO_2$ and $LiMn_2O_4$. The preliminary results indicate good stability over repeated charge-discharge cycles [*Chem Eng News*, **74** (24) (1996) p.8].   ❑

<div align="right">HKK</div>

Novel fan makes air flow faster

Terry Day of Darwin, Australia, has invented a Jet-fan, an unconventional device which produces five times more pressure than the conventional multi-blade fan.

Axial or centrifugal fans, with two or more blades, generate a strong air flow, but little pressure gain. High pressure can be achieved only by adding a diffuser, a large tubular device which uses up space, adds weight and cuts energy efficiency.

The Jet-fan, unique in itself, needs no diffuser, achieves high pressure build-up from between the trailing edges of its jet-style configuration, compresses the air, or liquids, and requires less power to operate. Also, it can be built in all sizes, from a miniature for the internal cooling of computers to a "jumbo" for power-generating turbines and jet aircraft engines.

The future work will be on the development of underwater uses for the fan.

For further information contact:

Mr Brian Bambach, Split Cycle Technology
7 Technology Drive, Arundel, Qld 4214.   ❑

<div align="right">HKK</div>

Prototype automotive device may replace catalytic converters

Researchers at the Pacific Northwest National Laboratory (PNNL) have developed a technique for treating automotive exhaust with electric current which may enhance the efficiency of cars' catalytic converters or even replace them altogether.

Electric corona discharges similar to what makes neon signs glow can cause reactions that break down harmful components in automotive exhaust. The technique has been developed to treat harmful vapours released during soil decontamination. It is now being tested by the PNNL researchers and "Big Three" engineers to assess its potential for treating vehicular emissions.

For further information contact:

Pacific Northwest National Laboratory
FAX: (509)375-2242.   ❑

HKK

Method to control shape of colloidal particles developed

Mostafa A El-Sayed and his colleagues at the Georgia Institute of Technology, Atlanta, USA, have developed a new method for synthesizing colloidal metal nanoparticles with shape control.

The method has been demonstrated for platinum and palladium neoparticles and is being extended to other metals. Shape control is vital in producing colloidal metal particles for catalysts and other high-tech uses because the particles' chemical reactivity depends on their size and shape.

It is observed that there has been virtually no work devoted to shape control of the particles, and shape control may be critical in some applications.

For platinum nanoparticles, sodium polyacrylate (a water-soluble capping polymer) was added to an aqueous solution of $K_2 Pt Cl_4$, then hydrogen was bubbled through the solution to achieve reduction *in situ* [*Science,* 272 (1996) p. 1924]. The nanoparticles' shape was controlled by adjusting the relative concentrations of capping polymer and platinum ions.

The Georgia Tech team dispersed the particle on amorphous carbon films and investigated particle structure with transmission electron microscopy. Low concentrations of sodium polyacrylate yielded predominantly cubic particles; higher levels gave mostly tetrahedral particles, and intermediate levels yielded mixtures of cubes and tetrahedra, with additional polyhedra and irregular prismatic particles.

The mechanism for shape-dependent synthesis is yet unknown. However, because both cubes and tetrahedra probably express the same, face-centered cubic struc-

ture, it is believed that the final shape is determined by relative growth rates on different crystal faces of the developing particle. The capping polymer functions to different degree on different faces of the basic structure, but it likely provides a kind of media viscosity control for the growth of the colloidal particles from solution.

Work is being done on several metals besides Pt and Pd, and it is hoped to deduce the mechanism by focusing on pH, ionic strength of the metal solutions, viscosity, and temperature [*Chem Eng News,* 74 (27) (1996) p. 9].   ❑

HKK

Taking yeast out of ethanol process

Peter Rogers and his team members at the University of New South Wales (UNSW) believe that ethanol can be produced faster and more efficiently by replacing yeast with the micro-organism *Zymomonas mobilis*. Presently, *Zymomonas* is being used to produce tequila, palm wines and other tropical beverages.

Ethanol is based on renewable resources. It involves the recycling of CO_2 and its use lowers emission levels of CO and other noxious gases. It can replace lead as an octane booster in petrol, factors which make it attractive for environmental and social reasons.

Rogers *et al.* have got funds from several US organisations and $5 million from Australian government, commercial sponsors, etc., with which they are setting up a pilot plant using new methods of producing ethanol from wastes from timber milling, the forestry industry and starch and sugar processing.

The combination of the pilot plant initiative and novel fermentation technology based on recombinant *Zymomonas* will lead to significant opportunities for new industries based on renewable energy resources [*Aust Sci Technol Newslett,* June 1996, p. 5].   ❑

HKK

Vapour membrane permeation method optimised

Researchers at the University of Technology, Vienna, Austria, have optimised a vapour membrane permeation method that can remove and recover the sulphides economically, at levels of 100ppm to 1000ppm.

The process involves selective removal of condensable components from gas streams by separation through polymeric membranes.

The driving force for the separation is a pressure difference between feed and permeate sides of the membrane, formed by pressuring the feed or applying a vacuum on the permeate side. A similar process is used to recover VOCs during the filling of fuel tanks.

The method was tested on a gas stream from a rayon fibre plant, using a transportable membrane laboratory test rig with *teflon* pipes and waste gas temperature control via a heat exchanger. The capillary composite membrane module was of a polydimethylsiloxane/polyether-sulphone type.

Concentrations of H_2S, CS_2 and water load were kept constant. Results showed the removal of CS_2 and H_2S depended on the load of the membrane surface, which varies with gas velocity and the concentration of the inlet gas.

At low membrane loads, over 90% CS_2 and 80% H_2S was removed. It was shown to be possible to meet $100mg/m^3$ if the membrane load was reduced but the required membrane area became very large. Removal efficiency at a membrane load of $40g/m^2h$ is 70-80% for CS_2. An increase of efficiency at the same membrane load could be realized by reducing the permeate pressure.

Carbon disulphide is explosive between 1-60 percentage volume, so attention is needed as regards to safety aspects [*Eur Chem News*, **65**(1716) (1996) p.22].   ❑

<div align="right">HKK</div>

Portable leak detector for refrigerant gases

Leaks of halons, FM200 and all chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC) refrigerants, in concentrations as low as 10 parts in 10^6 (10 parts per million), can be located with a hand-held easy-to-use portable leak detector from a British company at Lidbury (Sussex).

Measuring 220mm x 55mm x 35mm and weighing 370g, the Portamonitor (Halon) detector, from Lidbury, has its sensor mounted on a 250mm-long flexible spiral metal probe to make access possible to confined spaces or awkward locations. The detector is operated with one hand by means of an ON/OFF switch, two level sensitivity switch and a 'leak definition' control.

Leaks are detected by means of an ionizing DC negative corona principle, and leaks are indicated by an audible tone and four light-emitting diodes (LEDs) which illuminate progressively according to gas concentration.

The user simply switches the detector on and moves it around a valve joint or pipe, for example, until the leak site is identified. If a high concentration of gas causes the detector to alarm before the leak is located, the user switches the unit to a lower sensitivity level. This cancels the alarm and allows the detector to be moved closer to the leak site.

Microprocessor technology also enables the detector to take background levels of gas into account by means of the 'leak definition' feature, which stores a known level of gas concentration in its memory. When used in the 'leak definition' mode, the detector ignores the presence of gas up to the level stored in its memory and will only indicate higher gas concentrations, thereby allowing even large leak sources to be detected with pinpoint accuracy.

Power for the detector is provided by four standard 1.5V AA batteries, which provide a typical operating life of 40 hours per set. The detector is supplied complete with a carrying case [*BCN*(*Brit Com News, New Delhi*), Sept/Oct 1996, 7].   ❑

<div align="right">RS</div>

A novel internal body thermometer

A thermometer that can take the temperature of the body's delicate internal organs from outside the body has been developed by German scientists. It could help doctors pinpoint and treat tumours, which are warmer than healthy tissue. At present the only way to measure the temperature of internal organs is to insert a thermometer, and this is not practicable for organs such as the brain or liver.

Klaus Roth of the Free University of Berlin has developed a thermometer based on the rare earth element praseodymium and magnetic resonance imaging (MRI), a technique that is routinely used in hospitals for whole-body scanning. When the praseodymium compound is injected into the body, it absorbs and re-emits radio waves. The frequency of these radio waves varies with temperature.

Roth tested the praseodymium compound by injecting it into the bloodstream of an anaesthetised rat that was then gently warmed up on a water bed. He measured the rising temperature of the animal's liver by detecting changes in the frequency of the radio waves as the chemical passed through the organ. This is the first time anyone has measured temperature in this way in a live animal. It can now be developed for use in people.

The technique relies on nuclear magnetic resonance (NMR), the phenomenon on which body scanners are based. Hydrogen nuclei can take up two alternative quantum "spin" states. Radio waves can make the nuclei flip from one state to the other. The nuclei absorb and emit radio waves, enabling a scanner to pick up and chart the signals as peaks on a graph.

Roth's praseodymium compound is uniquely sensitive to temperature. In this experiment with the rat, Roth showed that the spectrum shifted according to the temperature. And the spectrum produced by the praseodymium compound could not be confused with the spectrum produced by the body's water molecules.

Roth, who developed the compound with scientists from Schering, the German pharmaceuticals company, expects the substance to be useful in cancer treatments which destroy tumours by heating them. The ability to monitor temperature during such treatments would make them safer and more precise.

Previous attempts to make internal body thermometers have failed because the compounds have either been too toxic or not sufficiently soluble in water to inject. Roth's compound is the first to overcome both limitations.

It could be useful in heat-treating tumours. It could also be useful for studying metabolism in inaccessible parts of the body. It might provide another way of monitoring brain function [New Sci, 150 (2020) (1996) 16]   ☐

Zeolite adsorbers can reduce automobile hydrocarbon emissions

A zeolite adsorber sandwiched between the two halves of a conventional automobile catalytic converter may be a cost-effective way to meet hydrocarbon emission standards for cold-engine start-up. The PUMA (passive underbody main adsorber) system, developed by Corning's environmental products divi-

sion, will cost less than the electrically preheated catalyst systems now being developed, according to a company spokesman. (The electrical systems are estimated to cost as much as $ 200 more than current conventional converters.) Upon engine start-up, cold exhaust gases are diverted through the adsorber, which selectively adsorbs the hydrocarbons and passes the remaining exhaust gases to the converter. The converter rises to operating temperature before the adsorber begins to release the hydrocarbons, which are then oxidized in the usual manner. In independent tests, a conventional 3.8-L engine using the PUMA system achieved hydrocarbon emissions of 0.03 g per mile, Corning says, which is well below the U.S. emissions requirement set for 2000. The system is also being adapted in Europe to meet the Euro-3 standards for the end of the century [Chem Eng News, 74 (11) (1996) 29].   ☐

Better nickel hydroxide battery

A new process for 'spherical' nickel hydroxide to improve the performance of rechargeable batteries has been developed by Bayer subsidiary H C Strack.

A new plant is under construction at Sarnia, Ontario, Canada, which will produce 2000 tonne/year of the new material from the beginning of 1997. The technology is also claimed to lead to a cleaner process as lower quantities of heavy metal particles are lost during the washing processes.

The spherical nickel hydroxide, consisting of microfine, round particles of an extremely narrow grain size distribution, has previously been produced in test quantities at a pilot plant facility at Starck's headquarters in Goslar, Germany.

Up to now, the nickel ingredient had only about two thirds of the theoretical storage capacity for electricity. With new material, a spherical nickel hydroxide, they are coming very close to 100 per cent.

The company estimates an electric car using the new material could travel some 200km before needing recharging. [Eur Chem News, 66 (1731) (1996) 22].   ☐

Fibre-optic device to measure tiny magnetic fields

Devising something small has always a charm and demand for some applications. Mini and nanoscale models in measuring magnetic fields are also coming into vogue. Such an urge has led a researcher, Richard

Wagreich at the University of Maryland to the optical bench. He has taken the clue to use ferrimagnetic materials to measure very tiny magnetic fields in a small space. His attempts are focussed on to measure very tiny magnetic fields using new optical geometry. Measurement of tiny magnetic fields is useful for biological applications particularly medical diagnostics. Two emerging applications are magnetoencephalograms which measure currents in the brain, and magnetocardiograms which measure electric current patterns in the heart.

Methods for measuring very small magnetic fields involve suspending superconducting quantum interference devices (SQUID) which are expensive to make and require supercooling. Magnetostriction is an optical method that does not involve cooling but the sensors are a few centimetres long. To get a high enough resolution, the sensor must be smaller relative to the object being measured.

Wagreich's scheme involves a fibre-optic sensor based on Faraday effect. Mirrors are arranged surrounding yttrium iron garnet (YIG), a ferrmagnetic material. Light is reflected back and forth through the mirror and then through the material and then through the lead-out fibre, where polarization is measured. When the magnetic field is present, the polarisation plane is rotated when the light passes through the YIG. The multiple passes produce more polarization rotation with less magnetic field which boosts sensitivity.

The prototype reported is a few mm long and detects magnetic fields of the order of nanotesla—less than a millionth of the Earth's magnetic field. Wagreich says that he aims at achieving at picotesla order but his immediate aim is to get the device off the bench.

The fibre optic magnetic field sensor does not need cooling, but it is very sensitive to vibration. Also alignment is the tricky part as in any fibre optic device.

For further details, contact George Gillespie, Assistant Director for Physical Sciences, Office of Technical Liaison, University of Maryland 4312, Knox Rd., College Park, Md.20742, USA [*Opt Photon News*, 7 (8) (1996) 11].   ❏

DSRM

Small-scale windpump

M/s IT Power, Eversley Hants RG27 OPR is involved in developing a prototype of water pumping wind mills, keeping in view of the fact that many available designs in the developing countries are inappropriate for production and sustainable small-scale use.

IT Power with industrial collaborators from Zimbabwe, Botswana, Indonesia, India and Mangolia has developed and tested a prototype machine at the Silsoe Campus of Cranfield University as the first phase of the project. The representatives from the six countries have assessed the prototype and discussed the opportunities for technology transfer.

In the new windpump, a different form of transmission is attempted which tries to overcome many of the disadvantages of a traditional gear box. It uses a small rotor diameter (earlier design by IT Power used 6-7.5 m rotor diameter) which results in faster speeds.

The transmission system is similar in principle to a double sided rack and pinion. The wind rotor turns the pinion on the rack, causing the rack to lift. At the top and bottom of the rack are semicircular gear teeth which move the rack over to the second side. The pinion then drives the rack down. In this way the rotational motion of the gearbox is translated into reciprocating motion, while at the same time providing speed reduction.

The design is the outcome of avoiding the past faulty design to meet the needs of farmers and small communities in developing countries. Though many designs tried earlier have sophisticated designs and contain specifically made cast components, they are heavy, and difficult to erect and maintain without considerable technical knowledge. Thus the technology transfer was difficult.

The second phase of the project, which began in May 1995 and is due to run for three years, will take the design from the prototype phase through to actual technology transfer to developing country manufacturers.

The new pump achieves a high level of performance and good reliability. It is a conventional, single acting, piston pump and is relatively simple to manufacture and maintain. Communities can depend on the new pump providing water on a reliable basis, reducing the demand for labor [*Technol Partnership Initiative News, London*, No. 9, 1996, p. 6].   ❏

DSRM

Flame length measuring instrument for aerosol industry

In aerosol industry experts have been studying the flame forerun and back flash of certain aerosol products. For this purpose, the flame jet test launched by IATA was used in which a candle and a tape are used. This test is more and more refined since then and is used as a routine test.

But there was a long-felt need in the aerosol industry for an instrument which gives reproducible results that are almost not subject to external factors.

The COMES company in Mohlin, Switzerland has reported such an apparatus called COMES FLM which has an electronic arc ignition, unlike the prevalent instruments which use Bunsen Burner. Thus no foreign gas will influence the tested spray jet and a falsification of the testing results is largely excluded. The instrument can pre-programme the spray time so that the flame tester can be triggered by remote control.

To document the flame forerun and/or flame jet back flash of the spray jet, the special ruler incorporated in the apparatus has flexible pointers marking the critical points as flammable/combustible.

Also, the COMES FLM has been equipped with an additional control device for an automatic instantaneous developing camera. It provides an immediate photographic documentation for the test series.

This flame measuring instrument is made up of Nirosta steel, and safe for practical use [*Aerosol, Eur*, **4** (1-2) (1996) 50-51].   ❏

DSRM

Tyre pressure monitor

A novel miniature remote-controlled monitor (7.6X2.5 cm) automobile tyres, has been developed by a British firm, Shrader Electronics Ltd, Antrim Technology Park, Antrim (N.Ireland). The monitor can provide a dash board read out to an accuracy of 1 psi (0.07 bar). The device is small enough to be fitted inside a tyre. It is actuated by a sensor.

The battery, which forms part of the sensor unit, took two-and-a-half years to develop and is now guaranteed to have a life of 10 years or 100,000 in mileage. Extensive testing was carried out in extreme weather conditions because temperatures inside a tyre can often reach up to 200°C.

Research and development work for the device costs more than £3 million. General Motors Corvette (UK) is expected to market the system for between $ 350 and $ 450. The manufacturers say they are working to reduce the cost for mass market cars with, perhaps, a less sophisticated system involving a flash warning light on the dashboard costing only about $ 20 a tyre, rather than an elaborate specific pressure readout.

They see another very attractive market in fitting the system to lorries and trucks although, in the case of the latter, there are problems involving the number of tyres and their relative distances from the driver's cab. Every major car company in the work has the product on test and some of the development costs have been recouped through the scale of prototypes. The manufacturers have advance orders worth $ 20 million from Europe and the USA. [*Spectrum*, (*Brit Sci Newslett*), **No. 254** Sept./Oct. 1996, p.1].   ❏

RS

New benchtop autoclave designed

A leading British firm, LTE Scientific Ltd, Greenfield, Oldham, Lancashire has developed a specially designed autoclave for sterilizing a wide variety of load types found in microbiological labs. Basically the device incorporates a microprocessor with a choice of 8 programmable cycles switchable from one load type to another.

The cycles handled by the autoclave typically include culture media, contaminated wastes, glassware and instruments, liquids and plastics wares and as a personal benchtop autoclave its rectangular stainless-steel work-chamber makes optimum use of the space available.

Its UK developers and manufacturers built the chamber to the stringent BS and American ASME code. Marketed as the Falcon 30 the model has 27 per ;cent more useful working capacity than cylindrical models of similar size. The microprocessor control system provides the accurate cycle reproducibility and traceability demand by today's laboratories.

With its easy-to-use system, the operator has only to press one key to select the desired cycle. From then on the process is completely automatic, with the sequential functions displayed on an illuminated mimic diagram and supporting status messages on a digital display.

An alphanumeric printer is fitted as standard. For ease of operation the autoclave is front-loading and safety devices prevent the door being opened until the pressure has dropped to atmospheric and temperature has reached a safe level.[*BCN (Brit Com News)*, Sept./Oct. 1996, p. 40]. ❏

RS

Protection against dangerous spillage

A novel coupling device 'APC Safety Breakaway Coupling' developed by Alpha Process Controls at Durham (UK) offers complete immunity against spillage of environmentally unacceptable emissions from road vehicles.

When vehicles move off or experience unstable conditions during the loading or discharging of flammable, toxic, and corrosive liquids, the APC Coupling provides an ultimate safeguard. The device fits between the flexible hose and the fixed installation, during loading or discharge by road, rail, sea, river and canal forms of transport such as tanker-lorries, ships and barges. A sister product is also available for use with loading arms.

Under normal conditions the coupling device allows free flow of product. However, in the event of an accidental tow-away or movement of the mobile equipment the coupling will separate and immediately seal off both ends with the minimum of spillage or damage. This ensures coupling integrity when assembled, while allowing the mating halves to break away effectively in an emergency situation. One of the advantages is that computer modelling of each customer's application gives a reliable determination of breakload.

Manufactured to the highest quality, with all parts having full traceability. The device is stainless steel as standard, but is available in Duplex, Hasteloy and Monel, in a variety of sizes with flanges integrally cast. It can be used in cryogenic applications because it can cope with very low temperatures [*BCN (Brit Com News, New Delhi)*, Sept./Oct. 1996, p. 40]. ❏

RS

Artificial skin minimizes scarring

Scientists at the Massachusetts Institute of Technology, USA, have developed an artificial skin which can be used on burn patients.

The material developed by Ioannis Yannas and his coworkers results in less scarring than from ungrafted burns or even autografts (skin transplants from donor sites on a person's body). Chemically bonding collagen taken from animal tendons with glycosaminoglycan (GAG) molecules from animal cartilage creates a simple version of the extracellular matrix that provides the basis for a new dermis, the underlying skin layer that does not regenerate when damaged. The collagen-GAG material has pores that permit cells to grow through the scaffold, making a new dermis as the scaffold is broken down by enzymes. Epidermis then grows over the area or is autografted.

For further information: e-mail Elizabeth Thomson at thomson@mit.edu or Circle 572. ❏

HKK

Magnets to deliver drug to the tumour

Inaccessible brain tumours might one day be cured by wearing an electromagnetic helmet that drives a tiny magnetic tugboat around the brain. The magnet, the size of a grain of rice, would also provide one of the least invasive ways to treat other brain diseases by ferrying drugs or radioactive implants to previously unreachable parts of the brain.

An American team unveiled the magnetic stereotaxis system (MSS). The first step is to make a three-dimensional map of the patient's brain using magnetic resonance imaging (MRI) scans. Doctors then map out the best path to a tumour, avoiding blood vessel's and sensitive areas of tissue.

Surgeons begin the operation by drilling a small hole in the patient's head and placing the magnet on the surface of the brain. The patient then dons, the magnetic helmet, which contains superconducting magnets. These are computer controlled to guide the magnet along the path mapped out by the doctors.

Although MRI scans give detailed pictures of the brain, they are too slow to monitor the progress of the implant during the operation. So the system relies on X-rays to highlight the position of the magnet and superimposes this image on the MRI map made earlier. Once at the tumour, the implant—for example, a radiation source—could remain in place for several days. The patient would then return to hospital to have it removed.

Washington University School of Medicine in ST Louis is testing the system with "brain boxes" — brain models composed of a clear gel-based substance. The models allow neurosurgeons to practice with the magnets, at Stereotaxis the start-up company which holds the patent on MSS. The system was developed by researchers at the universities of Washington and Iowa and the Medical College of Virginia.

Initial safety trials will be carried out on tumours that require a biopsy. In this case, the cargo will be one of several standard biopsy tools — for example, a tiny set of pincers that can clip tumour tissue and save it. The magnet and the tool will be attached to fine tethers, which can be used to gently pull them out.

Eventually, magnets could be used to deliver the drugs to treat a variety of conditions directly to affected brain tissue. For example, patients with Parkinson's disease might receive dopamine. Surgeons might also be able to reposition an existing implant so that patients could receive treatment directed at different parts of a tumour without enduring additional major surgery.

The system was greeted enthusiastically by neurologists. It's an innovative approach [New Sci, 149 (2023) (1996) 19].   ❑

Quick detection of disease with a dipstick

A plastic film that mimics litmus paper can instantly detect microorganisms that cause disease. The film changes from blue to red on contact with positive samples. All one needs is the ability to see colour. Deborah Charych, co-developed the test at the Lawrence Berkeley Laboratory in California.

The tests are based on polymers that change colour because bonds within the structure buckle on contact with target organisms or the toxins they make.

Doctors trying to identify infections often have to take samples from patients and culture them up until colonies of bacteria appear, but this can take longer than a week. Tests based on antibodies that cling exclusively to a target microorganism can take as little as 20 or 30 minutes, but they are often expensive and fiddly, requiring the addition of extra chemicals.

With this test, the signal output—the colour change—is directly linked to target recognition, one does not need any secondary reagents or fancy devices. It's just like a dipstick.   ❑

The developers base their "plastic litmus" on polymeric films that mimic the outer membrane of a living cell; The researchers are learning how to customize the polydiacetylene film to target different microorganisms and their toxins. They can detect the virus that causes influenza and the bacterial toxins that cause cholera and food poisoning, including botulism.

When made in the conventional way, polydiacetylene has a very ordered, crystalline structure. The crystals are brightly coloured because they contain an abundance of electron-rich carbon-to-carbon double bonds which absorb certain wavelengths of visible light. In the case of polydiacetylene, the bonds absorb redder frequencies, so the crystals look blue. But if they are stressed mechanically or by heating, the bonds buckle and absorb shorter, bluer wavelengths, so the crystals appear red.

The developers first make a thin film of the polymer by allowing it to assemble on the surface of water. The film is just like the surface membrane of a living cell, with one hydrophilic surface and the other hydrophobic.

They then link the same tree-like sugary molecules that protrude from real cell surfaces into the film. These sugary molecules provide critical docking points for viruses and bacterial toxins during infections.

For the flu virus test, for example, they wove in a synthetic version of the sugar molecule that the real flu virus binds to as it infects a cell. For the cholera test, they used a similar structure from gangliosides—the cell membranes in nerve cells that the cholera toxin binds to. When the toxins or organisms bind to the artificial docking points, they make the polymer buckle and change colour. It works even when the target is present in concentrations as low as a few parts per million.

The tests could be supplied as a film deposited on a glass slide, or as a suspension of liposomes—globules 100 nanometres across that are built from concentric layers of polymer.

The laboratory has applied for patents on the technology, and is negotiating with companies keen to develop it [New Sci, 149 (2020) (1996) 22].   ❑

New treatment to tackle arthritis

The neutron therapy already used to treat deep-seated cancers could provide a treatment for the debilitating inflammation of the joints seen in rheumatoid arthritis. If successful, the proposed therapy would be ten times cheaper than surgery and safer than other radiotherapies.

Jacquelyn Yanch of the Massachusetts Institute of Technology has developed the treatment to inject something into the joints that is not already radioactive but that will become radioactive for a very short time when it is bombarded with neutrons.

Rheumatoid arthritis occurs when the immune system attacks the synovial membrane that lines the joints. Anti-inflammatory cases, but where these drugs are not successful, the membrane has to be removed. In the US this is usually done surgically, but in Western Europe, Canada and Australia, doctors often inject radioactive particles into the lubricating fluid inside the joint. The particles emit radiation, which destroys the damaged membrane. This technique is not used in the US because of worries that radioactive particles might escape and cause damage elsewhere.

The MIT team plans to inject a nonradioactive drug loaded with boron into the affected area. Boron is excellent at capturing neutrons, and boron compounds are used in a similar way in neutron therapy for cancer. When a boron atom captures a neutron, it releases two high-energy particles.

The boron-loaded drug is absorbed selectively by the synovial membrane, which constantly purifies the synovial fluid by absorbing any particles floating around in it. The joint is then given a brief does of low-energy neutrons, which makes the boron briefly radioactive. It gives off high-speed particles that travel far enough to destroy the damaged membrane, but not far enough to harm tissue beyond the joint.

The treatment has been tested in human tissue removed surgically and kept alive in a laboratory. The next step will be to test the treatment in arthritic rabbits. Human trials are not expected for several years [*New Sci*, **150** (2024) (1996) 23].

Honours and Awards

Springer Elected to National Academy for Engineering

Karl J Springer, Vice President of the Automotive Products and Emissions Research Division at SwRI, has been elected to the National Academy of Engineering (NAE). Election to the NAE is among the highest professional distinctions accorded to an engineer.

The honour was received by Springer for his contribution to design of measurement and control systems to reduce smoke, odor, and other pollutants from diesel and gasoline engines.

Springer's career at the Institute began in 1957 and includes more than 30y of leadership in automotive emissions research. He is worldwide known for his pioneering efforts in control of air pollution from all types of motor vehicles. As Vice President of the Automotive Products and Emissions Research Division, he oversees a staff of almost 700 engaged in research, testing, and evaluation of diesel and gasoline engine lubricants, fuels, fluids, emissions, and of components for automotive, truck, bus, and tractor products.

Springer has authored 38 peer-reviewed technical papers and publications. He is a registered professional engineer in thestate of Texas, a Fellow of the American Society of Mechanical Engineers, a Fellow of the Society of Automotive Engineers, and a Diplomat of the American Academy of Environmental Engineers. In 1993, he was named to the academy of Distinguished Mechanical Engineering Graduates at Texas A & M University [*Technol Today*, 17(1) (Spring 1996) p.23].

HKK

Announcement

Habitat India 97 Exhibition and Conference

Exhibitions India in collaboration with Amsterdam Rai of Amsterdam and Jaarbeurs Utrecht of Netherlands will be organising HABITAT INDIA '97 exhibition and conference at Pragati Maidan, New Delhi, India during April 22-25, 1997. The event is coinciding with the "Earth Day" to celebrate and emphasize the importance of a constructive environmental policy.

The event will attract trade visitors from senior levels of central and state governments, and from public and private sector trade and industry, a veritable

who's who from the sub continent. Visitors will be looking for suppliers and providers of services to resolve the issues posed by the environment. Visitors to the event will be buyers, decision makers, senior executives, OEMs from the government and private sector companies; architects, planners, builders, plant managers, design engineers, consulting engineers, energy specialist and environmental consultants; senior management, both strategic and technical from all potential pollution sectors; buyers, specifiers, installers, managers of protection and security products and services; and civic agency officials involved with improving living environments.

Concurrent to the event there will be a high profile international technology conference covering living environment and related technologies and services.

HABITAT INDIA '97 is approved by The Ministry of Environment and Forests and supported by the Central Pollution Control Board, Tata Energy Research Institute and the Centre for Science & Environment.

The exhibition is open for trade only. For further information, please contact the following organiser:

EXHIBITIONS INDIA C-390, Defence Colony, New Delhi 110 024, India Tel: +91-11-462 2710/2711/1732/1760/3118 Fax: +91- 11-463 3506, 4648692, 462 3320 E-mail: india. exhibit@axcess.net.in Internet: exhibind@giasdl01.vsnl.net.in

Journal of Scientific & Industrial Research
(Incorporating *Research and Industry*)
Instructions to Contributors

The **Journal of Scientific & Industrial Research** (Incorporating *Research and Industry*) is published monthly to serve as an information link between the generators and users of technologies. It is addressed primarily to industrial entrepreneurs, technologists, engineers, technocrats and administrators in industry. Therefore, original research articles of practical interest to industry are invited for publication.

Contributions should have an economic bias, and wherever possible, cost estimates should be provided. They should be tersely written, giving only the significant results.

Besides, reviews on various branches of science and technology, science/industrial policy and management are also accepted.

Subject Coverage

Scientific Industrial Research

(i) Scientific investigations successful at the pilot-plant and in-plant trials.

(ii) Technology upgradation.

(iii) Development of cheaper and indigenous raw materials as replacement for uneconomical materials.

(iiv) Import substitution.

(v) Technologies for rural development.

(vi) Standardization and quality control.

(vii) Technologies of waste management.

(viii) Industrial R&D highlights.

Technology Management

(i) Success/failure stories in technology management.

(ii) Technology assessment.

(iii) Technology transfer.

(iv) Technology assimilation and adaption in different industries.

(v) Technology funding including venture capital.

(vi) Human Resource Development.

(vii) Management.

(viii) Environmental management.

Industrial Development

(i) Policies, programmes and progress.

(ii) Critical profiles of industries—individual and sectoral.

(iii) Technology Forecasting .

(iv) International Collaboration.

(v) Fiscal incentives aimed at industrial development.

Books, monographs and technical bulletins on industrial methods and techniques as well as other data like production and demand statistics are accepted for review.

A critical analysis of papers presented at any Indian as well as international technology seminar/symposium is also welcome.

Questions on the articles published in the journal, answers supplementing any of the published items, views, opinions, or suggestions on the various aspects of technology are welcome for inclusion in the column, 'readers react'.

The editors are keen in projecting the technology bottlenecks/problems faced by the industry for their solution by the scientists in various laboratories. They would welcome to be mediators between the industry and the laboratory.

Preparation of Manuscript

Manuscripts should be presented in electronic form as well as in hard copy. Pages should be numbered consecutively, and the matter should be arranged in the following order: title; name(s) of author(s); department(s) and institution(s); abstract; keywords; introduction; materials and methods; results and discussion; acknowledgement; and references. The abstract, tables and captions (for figures) should be typed on separate pages.

The electronic form of the manuscript should be submitted on a floppy disk of 5¼" (1.2 MB) or 3½ (1.44 MB) to the Editor along with one hardcopy print out and one xerox copy. Text of the manuscript may be entered using word processing softwares such as Word Perfect Version 5.5/6 or MS Word Version 6 (preferably on IBM compatibles) and for illustrations Corel Draw, Harvard Graphics or any compatible format software (BMP, GIF, JPG, PCX, TIF) may be used. Label the floppy disk with the author(s)' name(s), the word processing package, software for illustrations, and the type of computer. In case of discrepancy between the disk and the manuscript, the latter will be taken as the definitive version.

Title—The title, not exceeding about 50 characters, should be such as to be useful in indexing and information retrieval. If a paper forms part of a series, a subtitle indicating the aspect of the work covered in the paper should be provided. If the title is long, a short title suitable for use as running title should be supplied.

Name and Address—The names of all the authors with initials, if any, should be given along with the name(s) of institution where the work has been carried out. The present address of authors(s), if different from the place of work, should be given as footnote(s).

Abstract—The abstract, usually not exceeding 200 words, should indicate the scope and method used in the paper, highlighting the principal findings and conclusions.

Graphical Abstract—A short graphical abstract to be included in contents pages should also be submitted.

Keywords—Five to six in alphabetical order should be provided.

Introduction—The introductory part should be brief and state precisely the scope of the paper. Literature review should not exceed what is necessary to indicate the objectives of the research undertaken and the essential background.

Materials and Methods—New methods should be described in sufficient detail, but if the methods are already well known, a mere reference to them will do; deviations, if any, should however be stated.

Results and Discussion—Only such data as are essential for understanding the discussion and main conclusions emerging from the study should be included. Data should be arranged in a unified and coherent sequence so that the report develops clearly and logically. The data should be statistically analyzed, and the level of significance given. The same data should not be presented in both tabular and graphic forms.

The discussion should deal with the interpretation of results. It should relate the new findings to the known, and include logical deductions.

Acknowledgement—This should be brief and for special assistance only, not for routine 'permission' to publish, or such trivial formalities.

References—References to literature, numbered consecutively, should be placed at the end of the paper. In the text, they should be indicated by numbers placed above the line (superscript).

In citing *references to research papers*, names and initials of the authors should be followed, in order, by the title of the periodical in the abbreviated form (italics), the volume number (bold), the year within circular brackets and the first page reference ,e.g. Liotta R, Rose K & Hippo'E, *J Org Chem*, **46** (1981) 227.

For names of periodicals, the standard abbreviations listed in the *International Serials Catalogue* published by the International Council of Scientific Union's Abstracting Board should be used. If the reference is to an article published without any

authorship in a periodical, the title of the artilce takes the place of the author in the citation, e.g. Handloom Sector of Textile Industry in India, *J Mater Sci*, **18** (1983) 1443.

If a paper has been accepted for publication, the names and initials of the authors and the journal title should be given followed by the words "in press" within circular brackets, e.g. Chavan R B & Subramanian A, *J Sci Ind Res*, (in press).

Reference to a book should include, names and initials of authors, the title of the book (italics), name of publisher and place of publication within circular brackets, year and the particular page reference, e.g. Hearle J W S & Peters R H, *Fibre Structure* (The Textile Institute, Manchester) 1963, 91. If the reference is to the work of an author published in a book by a different author or edited by a different person, the fact that is cited from the source book (italics) should be clearly indicated, e.g. Karr C (Jr), cited in *Analytical Methods for Coal and Coke Products* by Karr C (Jr) (Academic Press, New York, London) **Vol. 1**, 1978, 7.

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Reference to a thesis should include the name of the author, title of the thesis (italics), university or institution to which it was submitted, and year of submission, e.g. Ghosh G, *Ph D Thesis. Structure of Coal*, Jadavpur University, Calcutta, India, 1984.

Reference to a patent should include names of patentees, country of origin (italics) and patent number, the organization to which the patent has been assigned within circular brackets, date of acceptance of the patent and reference to an abstracting periodical where available, e.g. Trepagnier J H, *U S Pat* 2.463. 219 (to *E I du Pont de Nemours & Co.*) 1 March 1949; *Chem Abstr*, **43** (1949) 7258.

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authors, the names of all the authors should be given. The abbreviations *et al., idem and ibid* should be avoided.

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Tables— These should be typed on separate sheets of paper without any text matter. They should be numbered consecutively in Arabic numerals and should bear brief titles. Column headings should be brief. Units of measurement should be abbreviated and placed below the headings. Negative result should be indicated as 'nil' and absence of data by a dash. Inclusion of structural formulae inside the tables should be avoided.

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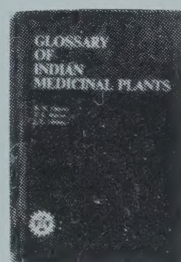
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